



UNIVERSITAT  
POLITÈCNICA  
DE VALÈNCIA

CAMPUS D'ALCOI



Politechnika  
Łódzka

## ***Master's degree in Textile Engineering***

Title:

"100% Bio-based microencapsulated phase change materials as regulator of temperature of textile fabric"

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February 2018

## **ACKNOWLEDGEMENTS**

This thesis would not have been possible without the generous support of the following people:

My tutor in Politechnika lodzka University of technology dr inż Lucyna Herczyńska, who was the guide in the process of developing this final master work.

All my teachers in my home University who gave new knowledge and due to this I could have the idea to develop in Poland.

My friends in Poland who became my family there meanwhile I was so far away from my family in México

My best friend Cesar Hernández who was not just a brother but also a guide and a support in this adventure we started two years ago.

To my girlfriend who has been so supportive since I started the Erasmus stance in Poland and also because I felt more motivated every day because of her.

Y por último y lo más importante en mi vida a mis padres que han sido mi guía desde que nací, gracias a ellos, Jorge López Hernández y Gloria Hernández Vargas, soy ahora lo que soy y me siento muy orgulloso de ellos, todo el apoyo que me han dado, desde lo económico hasta lo emocional es invaluable y toda mi vida estaré agradecido con ellos por haberme dado tanto.

## **ABSTRACT**

Phase change materials (PCM) are very useful in many fields due to their capacity to absorb and release heat energy when it is necessary. In this paper it was managed to microencapsulate 100% biodegradable PCMs to apply them into textile fiber in order to regulate its temperature.

There are many types of organic PCM with phase change temperatures from -5 ° C to 190 ° C. [1-5]. Solvent evaporation is a suitable technique to develop them [6]

The microencapsulation method used in the present work was solvent evaporation with oil-in-water emulsification. Scanning Electron Microscope (SEM) was conducted to confirm the successful microencapsulation. Differential Scanning Calorimeter (DSC) was used to evaluate thermal properties of the core material and also efficiency of the microencapsulation. Coconut oil and bee wax were used as PCM due to their melting point (Coconut oil - 23°C, Beeswax – 60°C) and, Polylactide (PLA) and Ethyl cellulose (EC) as shell materials because of their biodegradable nature. The microPCMs were applied onto the non-woven PLA with the help of a binder which in this case was calcium alginate and chitosan and then it was confirmed by SEM the microcapsules were inside the fabric and stick them to it. The thermal regulating properties of modified textiles were investigated by an IR camera. The results obtained from thermal analysis of samples showed that the temperature of the unmodified sample decreases faster than the modified sample.

**Key words:** Coconut oil, bee wax, polylactide, ethyl cellulose, chitosan.

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## **100% Bio-based Microencapsulated Phase Change Materials as regulator of temperature of Textile Fabric.**

### **1.0 CLASSIFICATION AND PROPERTIES OF PCM's.**

Phase Change Materials (PCMs) are substances that can absorb and release large quantity of latent heat energy during the change of their phase. This phase change depends on the specific melting point of the PCM and with it calculates the enthalpy of the reaction. Phase change materials (PCM) can be employed in many fields because of their capacity to absorb and release energy when it is necessary.

The ability of a PCM to absorb and release large amounts of energy has been the subject of study by many researchers who have tried to test it in many applications related to energy storage and thermal insulation.

There are many types of organic PCM with phase change temperatures from -5 ° C to 190 ° C. [1-5] It is very important to take into account the application of the PCM because that depends on the type that we are going to select. Normally materials with phase change below 15 ° C are used for cooling applications, materials with phase changes above 90 ° C are generally used for absorption refrigeration. Speaking of thermal comfort applications in textiles or building, PCM's and their mixtures are used with phase change temperatures between 18 ° and 65 ° C.

#### **1.1 CLASSIFICATION OF PCM's**

PCM's are classified in three types: organic, inorganic and eutectic, the important thing that must be taken into account is the amount of heat energy that PCM can store and also the temperature of phase change. Cabeza et al. [6] made a list of many pcm in their review where it was specified the type of pcm, the temperature of phase change, heat of fusion, thermal conductivity, density and their source.

##### **1.1.1 ORGANIC PHASE CHANGE MATERIALS**

Organic PCM's are divided into parafinics and not paraffinics which have the advantages of being chemical and thermal stable, not corrosive, can be recycled and do not present subcooling. However, the disadvantages of using organic PCM's are their flammability, their low thermal conductivity and the enthalpy of phase change is lower than other type of pcm.

##### **1.1.2 PARAFFIN WAXES.**

They consist mainly of a mixture of linear chains of n-alkanes,  $-\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$ , where the melting temperature, the enthalpy and the behavior of the specific heat capacity depends directly on the number of carbon atoms.

Research groups have studied the properties of paraffin waxes to develop heat storage materials. These studies have shown that paraffin waxes absorb, store and release a large amount of heat energy during the phase change between solids and liquids. they have high latent heat storage capacities between  $200 \text{ kJ Kg}^{-1}$  and  $250 \text{ kJ Kg}^{-1}$ , besides they are chemically inert, noncorrosive, odorless, long lasting, inexpensive, easily available, ecologically harmless and nontoxic [7,8,9-17].

### 1.1.3 POLYETHYLENE GLYCOL.

Polyethylene glycols (PEG), are composed of linear dimethyl ether chains with hydroxyl ending groups,  $\{\text{HO-CH}_2\text{-(CH}_2\text{-O-CH}_2\text{)}_n\text{-CH}_2\text{-OH}\}$ , these materials have been investigated in a variety of thermal storage applications for development of building envelopes to fabrics, foams and fibers and the principal advantages are high heat of fusion, low and moderate melting temperature intervals, low vapor pressure when melted, being chemically and thermally stable, nonflammable, biodegradable, non-toxic, non-corrosive and inexpensive

### 1.1.4 FATTY ACIDS AND FATTY ACID DERIVATIVES

The fat and oils of plants and animals are hydrolyzed to obtain mixtures of fatty acids which are purified and then separated. Fatty acids are among the few renewable materials and have properties comparable to paraffin waxes in PCM applications. They possess some better properties such as melting congruency, good thermal and chemical stability; they are non-toxic, biodegradable and suitable for many thermal energy storage applications because of their phase change temperature ranges.

Fatty acids and their eutectic mixtures are promising materials to obtain energy storage compounds due to their good thermal and physical properties and their easy impregnation in composite structures. Many of the fatty acids are commercially available because several industries already produce fatty acids in large quantities for plastics, cosmetics, textiles and other industries.

The disadvantages of fatty acids are that they have a bad odor, they are corrosive and especially they have a very high degree of sublimation. In order to enhance these disadvantages and obtain a better PCM with good thermal properties some fatty acids are prepared by esterification reaction between fatty acids and alcohols.

## 1.2 Inorganic Phase Change Materials.

The inorganic phase change materials are classified in hydrated salts, salts and metals. This type of materials has fewer advantages in comparison with organic materials. Some of them have a higher phase enthalpy, but these are corrosive, they have sub-cooling, phase segregation and do not have good thermal stability.

### 1.2.1 SALT HYDRATES.

Hydrated salts are defined as inorganic salts that have water molecules in a defined ratio as part of the crystal. These hydrated salts are in a solid state at room temperature and when they reach their melting point they begin to dissolve in their own water molecules.

### 1.2.2 SALTS.

These salts are used in applications that require a high temperature range although the latent heat enthalpy is lower than salt hydrates. An application in which these salts can be used taking advantage of its high temperature energy store is in a concentrated solar power plant, which uses this type of salts to store energy for later use.

### 1.2.3 METALS

In the category of metals as PCM, low melting metals and metal eutectics are included. These are good candidates for raising the temperature of the phase change due to its high heat of fusion per unit volume. This type of PCM has a very high thermal conductivity, low specific heat and low vapor pressure.

### 1.3 EUTECTICS.

Eutectics are a combination of chemical compounds that have a unique chemical composition and their solidification point is lower than any other composition obtained using the same components. These can be combined between organic-organic, organic-inorganic or inorganic-inorganic. This type of eutectic mixtures is suitable for use as PCM mainly in refrigeration applications..

## **2.0 METHODS OF MICROENCAPSULATION OF PCM's.**

### **2.1 STORAGE METHODS OF PCM's.**

The storage methods for the PCM are made in order to protect them from the environment, from the daily manipulation according to the type of application of this and to be applied in all kinds of materials such as buildings, textiles, bio-composites, composites and some others.

### **2.2 Microencapsulation of PCM's.**

Microencapsulation is a process in which solid particles, liquid or gaseous material is coated with a polymer. The term microcapsule refers to particles of micrometric size ranging from 1 micrometer to 1000 micrometers. The shell material of the capsules can be created by a wide variety of natural and synthetic polymer, depending on the chemical characteristics and intended use of the core, the conditions in which the product will be stored, the conditions of use to which the product will be exposed as well as cost and availability.



The morphology of the microcapsules will depend mainly on the core material and the encapsulation process of the material shell. The microcapsules can have regular or irregular form and these can be classified as follows:

- Mononuclear Type.
- Polynuclear Type
- Matrix Type.

The advantages of microencapsulation are that they protect unstable and sensitive materials from the environment, a better processing by improving the solubility and dispersibility of the core and the shell material, you can use a great variety of core material, production with a high concentration and high yield, shelf-life enhancement by preventing degradative reactions and evaporation, safe and convenient handling of core materials, masking of odor or taste.

These parameters describe the desired microcapsules:

- Particle size,
- Thickness and impermeability of capsule walls,
- Mechanical strength of capsule walls to withstand normal handling forces,
- Durability of capsule walls to temperature, humidity and various solvents,
- Functionality over numerous phase transition cycles,
- Good thermal conductivity with increasing heat-transfer area,
- Resistance to thermal stress for the whole product life, and (viii) the low cost.

## **2.3 Physical and mechanical processes.**

### 2.3.1 SOLVENT EVAPORATION

In this microencapsulation technique, the polymer must be dissolved in a volatile solvent, and mixed in a water-based emulsifying solution, in which the solvent must be evaporated, releasing the polymer that encloses the core material also dissolved in the solvent.

This technique is widely used in the pharmaceutical industries. Initially the coating solution is prepared by dissolving the coating polymer in a volatile solvent that is immiscible in the emulsifier solution. After that depending on the nature of the core material (hydrophobicity or hydrophilicity) it is dissolved or

dispersed in the polymeric coating solution. The mixture is added to the emulsifying solution with continuous stirring until the solvent is distributed in the aqueous phase and evaporated. At this point the material coat contracts around the core material and results in hardened microspheres [18].

### 2.3.2 SPRAY-DRYING.

The spray-drying technique is very used because it is a very cheap technique although it has some disadvantages such as the difficulty of controlling the particle size of the microcapsules, the energy consumed for the evaporation of a large amount of aqueous phase and the moderate yield of the capsules produced.

This microencapsulation technique is carried out spraying the feed solution or emulsion in small droplets using an atomizer, then placing the previous dispersion in contact with the gas stream at the temperature necessary for the complete evaporation of the solvent, separating the solid particles carried by the gas phase with cyclones and filters. Shell materials like polysaccharides, such as gum acacia, hydrophobically modified starch, alginate and carboxymethylcellulose, and proteins, such as whey proteins, soy proteins and sodium caseinate.

### 2.3.3 FLUIDIZED-BED.

The fluidized-bed technique is carried out by spraying the coating material in the form of a solution or by melting in hot air on solid particles suspended in a stream of heated gases, generally air. It can coat a lot of different particles, including irregularly shaped particles. This technology is mainly used to encapsulate solids for pharmaceutical products.

The coating materials can be hydrocolloids and polymers. This technique generally produces microcapsules between 100 and 150 Micrometers.

### 2.3.4 CENTRIFUGAL EXTRUSION.

This technique is widely used in the food industry [19]. In this process two mutually immiscible liquids, which will be the core and the shell material, are pumped through a two fluid nozzle that is centrifuged in a very fast way. The column of the two produced fluids spontaneously breaks up into droplets and each drop contains a central region surrounded by a continuous film of fluidized shell material after the shell is solidified by cooling or by immersion in a gelling bath and thereby producing the microcapsules.

## **2.4 Chemical processes.**

### 2.4.1 IN SITU POLYMERIZATION.

In situ polymerization is a technique with which you can produce micro and nano capsules and particles. These processes have the capacity to produce microcapsules with the best quality in terms of diffusion-tightness of their walls.

In this technique the first thing you have to do is to disperse a liquid immiscible in water or material of solid core in an aqueous phase that contains monomers that will react with each other around the core material to establish solid condensation polymer shells that can be polyamide, polyester, polyurethane or similar substances.

In some cases the aqueous phase also contains an anionic surfactant to modify the system in a way that improves the deposition of the polymer shell. Formation of the shell occurs once the aldehyde-type monomer is added and an acid is added to the aqueous phase to obtain a pH between 2 and 4.5. Or the prepolymer self-condenses around the drop of core material in relation to its surface activity. This technique has the peculiarity that the polymerization occurs in the aqueous phase thus producing a condensation product that is deposited on the surface of the material of the dispersed core where the polymerization continues.

This in the end produces a very well crosslinked and insoluble capsule shell in water. The polycondensation reaction occurs completely on the side of the aqueous phase of the interface, which is why the reactive agents do not have to dissolve in the core material. The individual microcapsules prepared with this technique are spherical in shape and can have diameters of between 1 and 100 micrometers.

### 2.4.1 INTERFACIAL POLYCONDENSATION.

Interfacial polycondensation is a technique in which a microcapsule wall of a polymer is formed at the interface of a two-phase solution. These different phases contain a specific monomer dissolved and prepared to react with a monomer present in the other phase. First, a multifunctional monomer is dissolved, which can be an aliphatic diisocyanate in the organic core material. Then the resulting organic mixture is dispersed in an aqueous phase which contains a mixture of emulsifiers which could be PVA (polyvinyl alcohol) and a salt of lignin sulfonate, and protective colloidal stabilizers. After that a reactive multifunctional amine or a combination of amines is added to the aqueous phase.

The reactive amine diffuses along the interface between the organic and aqueous phases, where the polycondensation reaction is carried out with the multifunctional monomer in the presence of an acid catalyst, this results in the formation of the polymer shell which is insoluble in the two phases. The wall of the polymeric cover, typically polyester, polyamide and polyurea, which is formed at the interface separates from the aqueous phase and is deposited on the surface of the dispersed droplets of the core material, encapsulating it in this way. Once the reaction is initiated the material shell becomes a diffusion barrier and limits the interfacial polymerization rate. The size of the particle can be controlled by the speed and also depending on the emulsifier used.

In this process you can obtain particle sizes ranging from 1 Micrometer to 100 Micrometer in diameter [20–25]. One drawback to the technology for some applications is that reactive molecules dissolved in the core can react with the core materials. [24].

## **2.5 Physicochemical processes.**

These physicochemical techniques are based on the separation of the phases of a colloidal system, in which a soluble envelope material is added around the core material to form a solid wall, for example coacervation and evaporation of solvent [26,27]. H.G. Bungenberg de Jong y H. Krut worked with this technique and performed the first phase separation approach, also called a phase separation phenomenon such as coacervation [28,29]. IUPAC defines coacervation as the separation of a mixture into two liquid phases in the form of colloidal systems of water in oil or oil in water [30]. There are two methods for coacervation and these are the simple and the complex.

The microcapsules obtained usually get high heat capacities of about 145–240  $\text{kJ kg}^{-1}$ . The main limitation of this approach is the difficulty in scale up of the process [26,31].

## **3.0 CHARACTERIZATION OF MICROCAPSULES WITH PCM.**

### **3.1 Optical microscopy (OM).**

This technique provides images with good resolution to see if there are microcapsules in a solution or even with dry powder in powder. You can see also the morphology but it is so hard to see other specific details about the shell, besides you can see the type of microcapsules that we have in the solution like mononuclear, polynuclear or this kind of characteristics.

### **3.2 Scanning electron microscopy (SEM)**

This instrumental technique is very used and essential for the characterization of microcapsules, with this technique you can observe the morphology of the microcapsules besides you can measure the microcapsule diameters by using the images of this technique provides.

You can also observe if the MicroPCM is completely clean or it has some residue from some substance of the microencapsulation process or if the surface has porous or is smooth.

### **3.3 Differential scanning calorimeter (DSC)**

This technique is used to know the amount of latent heat that is necessary for the PCM or microcapsules to change phase by measuring the endothermic and exothermic transitions as a function of temperature. It can also measure specific heat capacities [32]. For this reason it is an essential tool in the study of thermal properties of the material, you can also obtain melting and solidifying temperature, as well as, revealing if the material has a good capacity to store energy.

### **3.4 Thermogravimetical analysis (TGA).**

Thermogravimetical analysis measures the amount and degree of change in the weight of a material as a function of temperature or time in a controlled atmosphere. These data are mainly used to know the composition of the materials and to predict their thermal stability.

The technique characterizes materials that exhibit weight loss or gain due to decomposition, oxidation or dehydration and also to their thermal stability.

## **4.0 TEXTILE AND CLOTHING APPLICATIONS OF PCM's.**

Textile products and clothing have been fundamental materials for the human being to feel comfortable and protected against certain external factors and thus ensure that the physical conditions of our body are adequate for survival. This protection can comprise a series of functions, maintaining the appropriate environment for the body [33-39]. One of the main functions of clothing is to protect the body from the climate by creating a microclimate-stable next to the skin to support the system of thermal regularity of the body for which the textile fibers must have certain properties.

Some of the properties included in clothing materials are thermal conductivity, thermal insulation and the transfer of heat between the body and clothing depending on the environment. Other properties involved are the thermal properties, the air permeability, the moisture vapor and the moisture recovery of the materials influence the hermetic balance of the body and, consequently,

affect the comfort of the clothes [33-39]. The thermal insulation of the materials can be obtained by means of passive or active insulating materials. These passive thermal insulators are those that function as thermal insulators thanks to their natural structure or some special design in which the fibers or threads are arranged in a way to prevent the passage of temperature.

A thermally passive insulator is one that is incorporated with certain materials specialized in the abstraction of heat such as PCM that have a cushioning effect against changes in temperature, these textiles can absorb heat from the human body or the environment at high levels of activity or in hot climates and also on the contrary they can release heat in cold environments.

There are many PCMs with phase change temperatures in ranges between 18 ° C and 35 ° C that were used for thermal comfort of humans. Paraffin waxes, especially n-eicosane [40,41], n-octadecane [40-50] and n-hexadecane [40,42-44,51-52] they are preferred for the application in textiles due to their high latent heat in phase change, the intervals of the phase change temperature, furthermore they are chemically inert, non-toxic, non-corrosive and non-hygroscopic. Furthermore, some of the binary mixtures, e.g. n-tetradecane/n-hexadecane [49] and n-hexadecane/n-eicosane [40,53,54], They have been applied in textiles. The use of binary mixture allows to extend the temperature range and can be used in textile applications [53,54].

#### **4.1 Incorporation of microencapsulated PCMs to fibers, fabrics and foams.**

The application of pcm in textiles brings many advantages for example: they are very easy to apply to textiles, fabrics, nonwovens and fibers, they usually do not affect the properties that the textile already has, they have a shelflife on a garment that permits normal fabric-care processes, they promote mixing of core materials, they reduce the reactivity of the PCMs with the external environment, they decrease the evaporation of the core material to the outside environment, they increase the area of heat transfer and they provide a constant volume in the core material [34,55-56]. The composition of the material shell and the amount of microcapsules added to the structure are the main factors that provide a suitable management in the textile product. When a sufficient amount of microPCM is added to a textile structure as a suitable component for coating of fabric, fibers, yarns and breathable foams a suitable thermal management in the textile product, which satisfies the end-use needs for which it was created. These will continue to function as long as the coating or the fibers remain intact otherwise the properties provided will be lost [57-58].

## **4.2 Incorporation of microencapsulated PCMs into the matrix of fibers**

The incorporation of microPCM's into the matrix of artificial and synthetic fibers can be achieved by wet spinning for polyacrylonitrile [59-60], polyacrylonitrile–vinylidene chloride [50], acrylic fiber [61], and by melt spinning [60] for polypropylene [62] or polyethylene fiber [47]. The advantages of embedding microPCM's in the structure of the fiber are the durability of the microcapsules will be greater being inside the fiber without showing any change in the physical appearance of the fiber only will be noticed a change to the touch, fall, smoothness and color in the finished fabric, however, the thermal heat capacity of the fibers obtained is limited to a load content of the microPCM's ranging between 5 and 10% by weight. In addition, the conditions of the process can damage the shell of the microcapsules and the formation of groups of particles can alter the thermodynamic properties of the fibers [59,63-66].

## **4.3 Incorporation of microencapsulated PCMs to fibers and fabrics by coating**

Y.G. Bryant and D.P. Colvin [67-68], and later D.P. Colvin and Y.G. Bryant [35] developed new methods to place microPCM into textile products in different ways to overcome the difficulty of incorporating enough microPCM in the fiber structure and improving the thermal properties, while maintaining the mechanical characteristics of the fiber. They added MicroPCMs to a binder and then they applied this binder with microPCMs as a coating to fibers and fabric [63].

Many textile applications were made, such as thermal barriers with microPCMs for insulating pads, footwear sneakers [63], cold water diving clothes [64], leather products with microPCMs [69-71], fabric sheets with shaped channels filled with microPCMs [72], improved fire clothing, military uniforms, gloves and shoes [73-74], and textile products that have electronic heating circuits in their interior in supports with microPCMs [75].

The polymer binder may be in the form of a solution, dispersion or emulsion in water or in an organic solvent. For most garment applications, an elastomeric polymer with a glass transition temperature varying from about  $-30\text{ }^{\circ}\text{C}$  to about  $+12\text{ }^{\circ}\text{C}$  is preferred [35,67-68,76-77]. However, the fabric and articles became stiff and moisture-impermeable, thereby reduced the fabric softness, flexibility, breathability and moisture transport properties. These reduced properties of such a continuously microPCMs-coated fabric can detract from the comfort of a person wearing a garment which is made from this fabric [56].

#### **4.4 Incorporation of microencapsulated PCMs to foams.**

The method for manufacturing foam with organic pcm of paraffinic base (n-alkane) with melting temperature ranges between 13 and 27 ° C was first described by Y.G. Bryant and D.P. Colvin in 1996 [67]. They added between 20 and 60% by weight of microPCM to the prepolymer mixture before curing and mixed therein to ensure wetting and the same dispersion throughout the mixture. the microcapsules were embedded within a polymeric matrix so that they were distributed individually throughout the foam. This foam could be used in thermal insulation applications such as a lining for gloves, footwear, interiors of vehicles, or any other where thermal insulation is required.

The advantages of this technique are that it can incorporate a large amount of microPCM with several formulations of PCM, in a foam matrix [67,68]. M.L. Nuckols studied the thermal performance of existing insulating foams in the market such as microPCM in dry suit systems, and obtained an analytical model to compare the relative thermal performances of improved dry suits with existing dry suits in the market [64].

He concluded that the dry suit containing microPCMs could reduce the heat loss of the diver in the initial phase of a dive by releasing the latent energy stored in the microcapsules. The effect of this release of energy was a delay in cold temperatures through the diver's suit, resulting in lower temperature gradients inside the suit. This delay could last until the PCM core material of the microcapsule changes phase to solid state and at that point the foam behaves like conventional suit insulation [64].

#### **4.5 Performance testing of PCM incorporated textiles and clothing.**

T.L. Vigo y J.S. Bruno preliminarily measured the thermal regulation properties of textiles with PCM using IRT [32], this system connected with a thermal vision camera, is a device used for thermal, accurate evaluation and provides images that represent surface temperatures by measuring the magnitude of the radiation infrared emitted from the surface of an object. In this method the surface to be tested is heated using regulated heating sources, and the thermal chamber monitors the resulting thermal transient on the surface [32]. Another method for the evaluation of smart textiles with microPCMs has been developed by M.M. Michalak et al. [18] which is based on temperature measurements of the simultaneous thermovision on both sides of the material during the process of temperature change either heating or cooling.

In their review article F. Agyenim et al. mention that there is a lack of international standards for testing and analysis used in the improvement of thermal energy storage systems [60]. As a consequence of this many research groups apply different approaches in test and analysis procedures that are related to temperature regulating properties in fabrics containing PCMs.



## 5.0 EXPERIMENTAL PART

In the present paper is shown the procedure to microencapsulate organic phase change material (bee wax and coconut oil) by interphase precipitation during evaporation of the solvent from water/oil emulsion. 100% biodegradable polymer materials were used as shell (Poly(lactic acid) (PLA) and Ethyl cellulose (EC)).

### 5.1 Materials and Method.

#### 5.1.1 MATERIALS.

Materials used for the microencapsulation were as follows:

- Coconut Oil as phase change material - commercial product.
- Beeswax as phase change material - commercial product.
- Different sort of Poly(lactic acid) (PLA) as shell material – a commercial product of NatureWorks®LLC
  - PLA 4060D - a amorphous resin
  - PLA 6201D - a thermoplastic fiber-grade resin
  - PLA 6400D - thermoplastic fiber-grade resin
- Ethyl cellulose (EC) as shell material - a commercial product manufactured by Aldrich (4cP viscosity measured for 5% toluene/ethanol 80:20 solution).
- Dichloromethane, chloroform, ethyl acetate were used as organic solvent - a commercial product manufactured by Chempur.
- Poly(vinyl alcohol) (PVA) (Mw = 1000, manufactured by Aldrich) as a surfactant/emulsifier.
- For the coating of the PCM microcapsules on textile a coating binder was used as follows:
  - Sodium alginate (ALDRICH product of 15-20 cP viscosity, (1% solution in H<sub>2</sub>O, temperature 25°C)) at a 1,5% w/w. concentration of in aqueous solution, and 10% w/w. calcium chloride dihydrate (Chempur) solution – as a coagulant.
  - Chitosan (ALDRICH product of 200-800 cP viscosity, (1 wt.% in 1% acetic acid, 25°C) at a 1% w/w. concentration of in 1% acetic acid solution.

- Polylactide nonwoven (a commercial product manufactured by FET Taiwan, SLN-2539W5, 1,5 den/38 mm FB) was applied for the modification with PCM microcapsules.

#### 5.1.2 MICROCAPSULES PREPARATION.

Microcapsules with polylactide or ethyl cellulose shell were obtained by solvent diffusion from the emulsion. Solvent evaporation is a physical method in which basically the polymer (shell material of the microcapsule) and/or core material are dissolved in oil phase and put in a emulsification mean (water phase) with an specific rotation speed. The oil-in-water emulsion was obtained by homogenization of the organic phase (polylactide or ethyl cellulose and coconut oil or bee wax in organic solvent) in the aqueous phase containing a surfactant/emulsifier – 1% solution of poly(vinyl alcohol). In this technique, a poly(vinyl alcohol )(PVA) emulsifier is used to reduce the interfacial tension between the dispersed droplets and the continuation phase, in addition to protecting the droplets from aggregation.

The microcapsules were created after complete removal of the solvent from the droplets by evaporation during the mixing process. The manufactured microcapsules were washed, decanted and dried. The conditions of encapsulations process are presented in Table 1 and 2.

Optimal conditions to obtain microcapsules with different kind of core material were achieved by modifying the conditions of the forming process. Among the effective parameters affecting the microcapsule preparation process can be mentioned: the type and amount of polymer used as the shell layer, the type and amount of core material, the rate of homogenization or the type of solvent used. These studies have allowed to optimize the conditions of the microcapsule production process with the desired properties.

**Table 1.**Name of Samples and amount of materials used in its elaboration.

NAME	AMOUNT OF POLYMER		AMOUNT OF SOLVENT		PCM	
	TYPE OF POLYMER	POLYMER (g)	SOLVENT	SOLVENT (ml)	TYPE OF PCM	AMOUNT (g)
COPLA3	PLA 4060D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA5	PLA 6400D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA6	PLA 6201D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA8	PLA 6201D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA11	PLA 6201D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA14	PLA 6201D	0.75	METHYLENE CHLORIDE	5	COCO OIL	0.2
COPLA18	PLA 6201D	0.40	CHLOROFORM	10	COCO OIL	0.2
COPLA19	PLA 6201D	0.40	METHYLENE CHLORIDE	10	COCO OIL	0.2
COPLA20	PLA 6201D	0.40	METHYLENE CHLORIDE	10	COCO OIL	0.2
COPLA21	PLA 6201D	0.40	CHLOROFORM	10	COCO OIL	0.2
COEC1	ETHYL-CELULOSE	0.40	CHLOROFORM	10	COCO OIL	0.2
COEC2	ETHYL-CELULOSE	0.40	METHYLENE CHLORIDE	10	COCO OIL	0.2
COEC3	ETHYL-CELULOSE	0.40	CHLOROFORM	10	COCO OIL	0.2
COEC4	ETHYL-CELULOSE	0.40	METHYLENE CHLORIDE	10	COCO OIL	0.2

**Table 2.**Name of the samples prepared with Bee Wax as core material.

NAME	AMOUNT OF POLYMER		AMOUNT OF SOLVENT		PCM	
	TYPE OF POLYMER	POLYMER (g)	SOLVENT	SOLVENT (ml)	TYPE OF PCM	AMOUNT (g)
BWPLA1	PLA 6201D	0.40	CHLOROFORM	10	BEE WAX	0.2
BWEC2	ETHYL-CELULOSE	0.40	CHLOROFORM	10	BEE WAX	0.2
BWPLA2	PLA 6201D	0.40	CHLOROFORM	10	BEE WAX	0.2
BWPLA3	PLA 6201D	0.80	METHYLENE CHLORIDE	10	BEE WAX	0.2
BWEC3	ETHYL-CELULOSE	0.80	CHLOROFORM	10	BEE WAX	0.2
BWEC4	ETHYL-CELULOSE	0.40	CHLOROFORM	5	BEE WAX	0.1
BWPLA4	PLA 6201D	0.40	CHLOROFORM	8	BEE WAX	0.2
BWEC5	ETHYL-CELULOSE	0.55	CHLOROFORM	10	BEE WAX	0.15
BWEC6	ETHYL-CELULOSE	0.55	ETHYL-ACETATE	10	BEE WAX	0.15

### 5.1.3 METHOD OF CHARACTERIZATION OF MPCM'S.

#### 5.1.3.1 Scanning Electron Microscopy (SEM).

The surface structure of the obtained microcapsules was analyzed using microphotography obtained by means of the High-resolution electron microscope Nova Nanosem 230 and Scanning electron microscope JSM-5200LV (JEOL). The observations were carried out under high conditions at 10 kV and different magnifications.

This technique it was also used to make the measurements of the microcapsules diameter.

#### 5.1.3.2 Differential Scanning Calorimeter (DSC).

DSC measurements were done on a differential calorimetry of TA Instruments Thermal Analysis -- DSC Standard Cell RC equipped with a refrigerated cooling system. DSC analyses were conducted under a nitrogen atmosphere and the temperature interval cycle was set to -40 - 40°C (Coconut Oil) or 0 – 80°C (Bee wax) at 10°C/min. The tests were made in order to identify the thermal capacity and phase change enthalpy values. The latent heat capacity of the Bio-based PCM microcapsules was determined by calculating of the area under the peaks that represent the solid–solid and solid–liquid phase transitions. Moreover DSC gave the melting point of the core materials thereby it could know the temperature which they would start to absorb or release heat energy depending on the cooling or heating process.

#### 5.1.3.3 Infrared thermography.

Infrared thermography was used to investigate the thermal changes in the fabric, i.e. the temperature distribution but also the thermoregulation effect. Thermo-graphic camera is used to measure the amount of heat energy that some material releases and the most important thing is how it decreases or increases the temperature of that material after time.

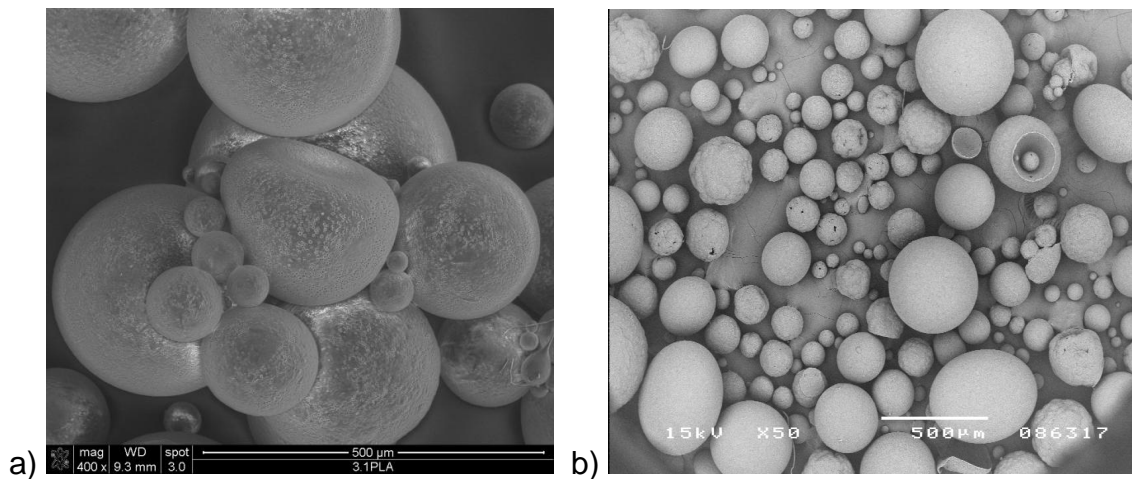
In addition, this technique provides visual information of the temperature changes that are occurring in the material that has been exposed to temperature, either low or high.

#### 5.1.4 CHARACTERIZATION OF MICROCAPSULES WITH COCONUT OIL OR BEE WAX .

The morphology, chemical structures, and thermal properties of the microcapsules with PCM were analyzed to evaluate their characteristics.

#### 5.1.4.1 The effect of polylactide type.

There are many types of PLA depending on the proportion of the crystalline phase. Three kinds of polylactides, two completely amorphous (PLA 4060 and 6400) and one with a small proportion of crystalline phase (PLA 6201 D) were used in the work. On the basis of microscopic images (Figure 1), microcapsules have a spherical shape regardless of the type of polymer used. If a completely amorphous polymer is used, the microcapsules are characterized by a more porous surface (Figure 1a)). In addition, a large amount of polymer in the form of a film was also observed during the microcapsule production process. That is why it was decided to use the PLA 6201D polymer as the most viable option for this procedure.

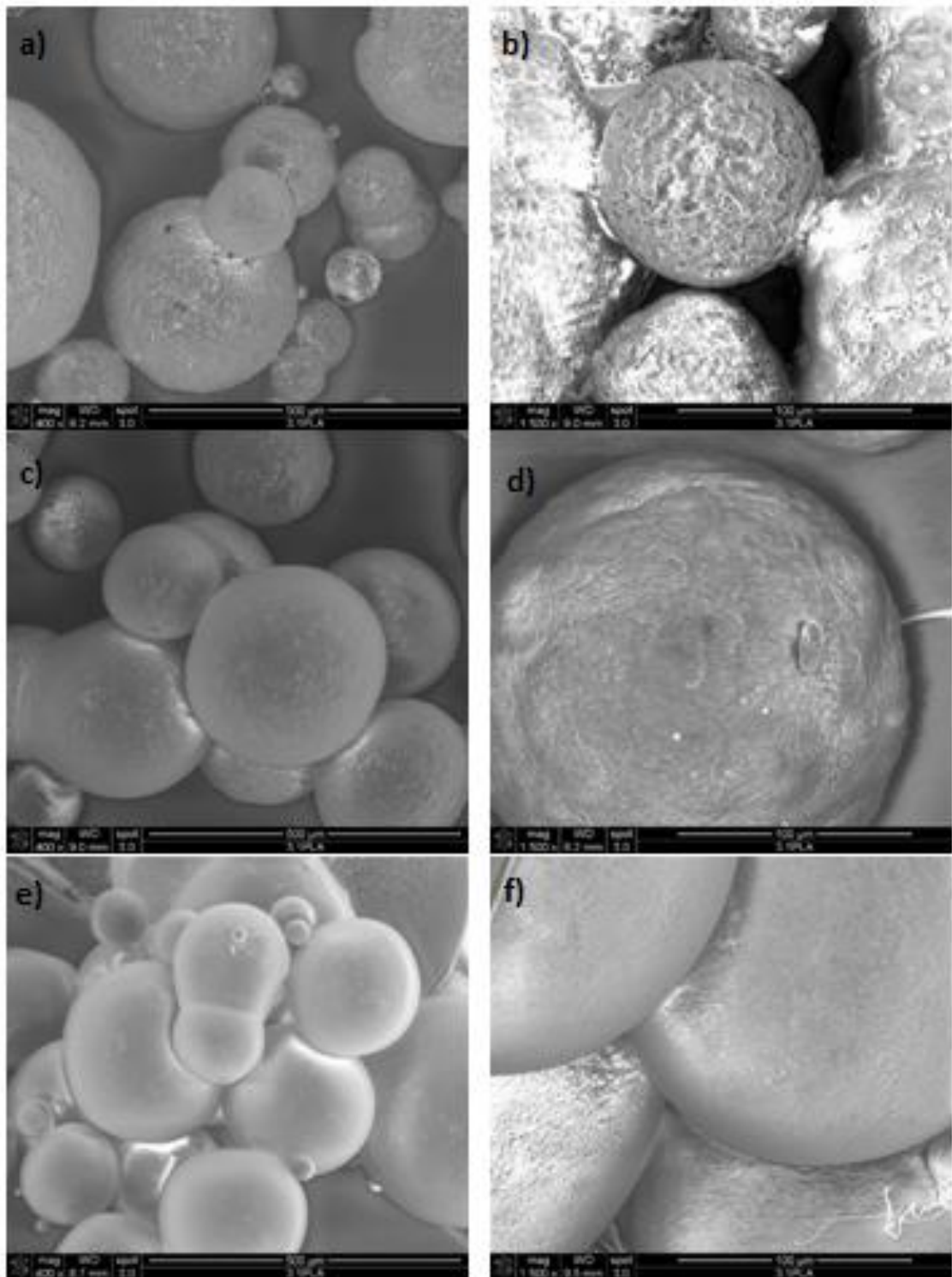


**Figure 1.** SEM images of: (a) sample COPLA3 made with PLA 4060D and (b) sample COPLA14 made with PLA 6201D.

#### 5.1.4.2 Influence of mixing speed on the encapsulation process.

The speed of stirring is very important in the process of creating microcapsules. The mixing speed affects the size of the capsules that are formed, as well as the morphology of their surface. Three tests were performed at 600 rpm, 900 rpm and 1000 rpm and the results obtained were as follows.

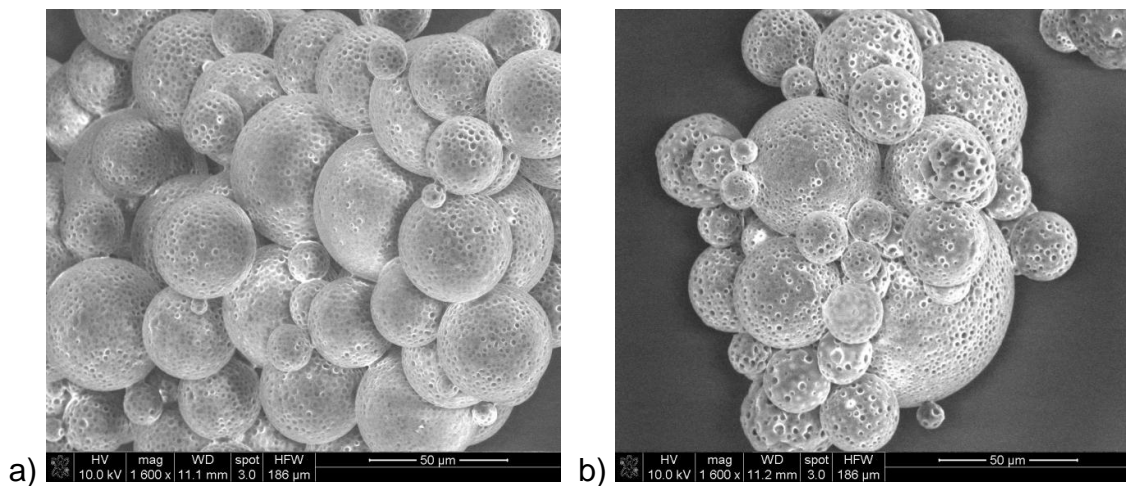
It can be observed in Figure 2 that reducing the speed of homogenization resulted in rougher surfaces. By comparing Fig. 2a to Fig. 2f, it can be observed that the sphericity and surface morphology of microcapsules were affected by changing the mixing speed from 600rpm to 1000rpm in the emulsion. Reducing the speed of homogenization would increase the viscosity of the dispersed phase, and thereby lead to porous surface of capsules.



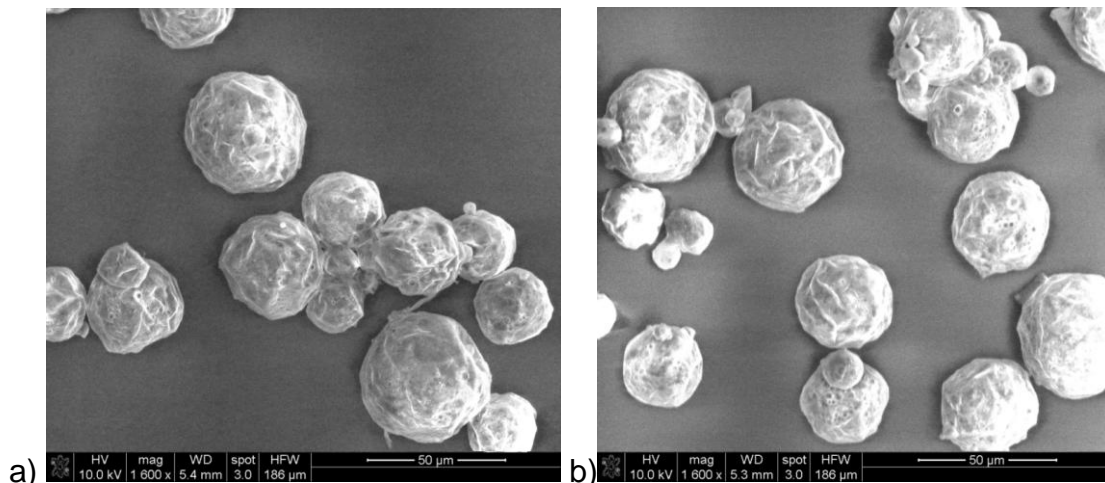
**Figure 2.** SEM images of the samples (a, b) COPLA 8, (c, d) COPLA 6, and (e, f) COPLA 11 that obtained at the speed of mixing 600 rpm, 900rpm and 1000rpm, respectively.

#### 5.1.4.3 Influence of solvent type on the encapsulation process.

Three types of solvents were used in the tests (chloroform, methylene chloride and ethyl acetate). Figure 3b shows the microcapsules with a more porous surface with respect to the microcapsules obtained with the participation of chloroform (Fig.3a). This is probably due to the lower boiling point of methylene chloride which results in a faster evaporation process of the solvent affecting the formation of the porous structure. When using solvents with similar boiling point, we do not observe any significant changes in the morphology of the microcapsules obtained (Figure 4).



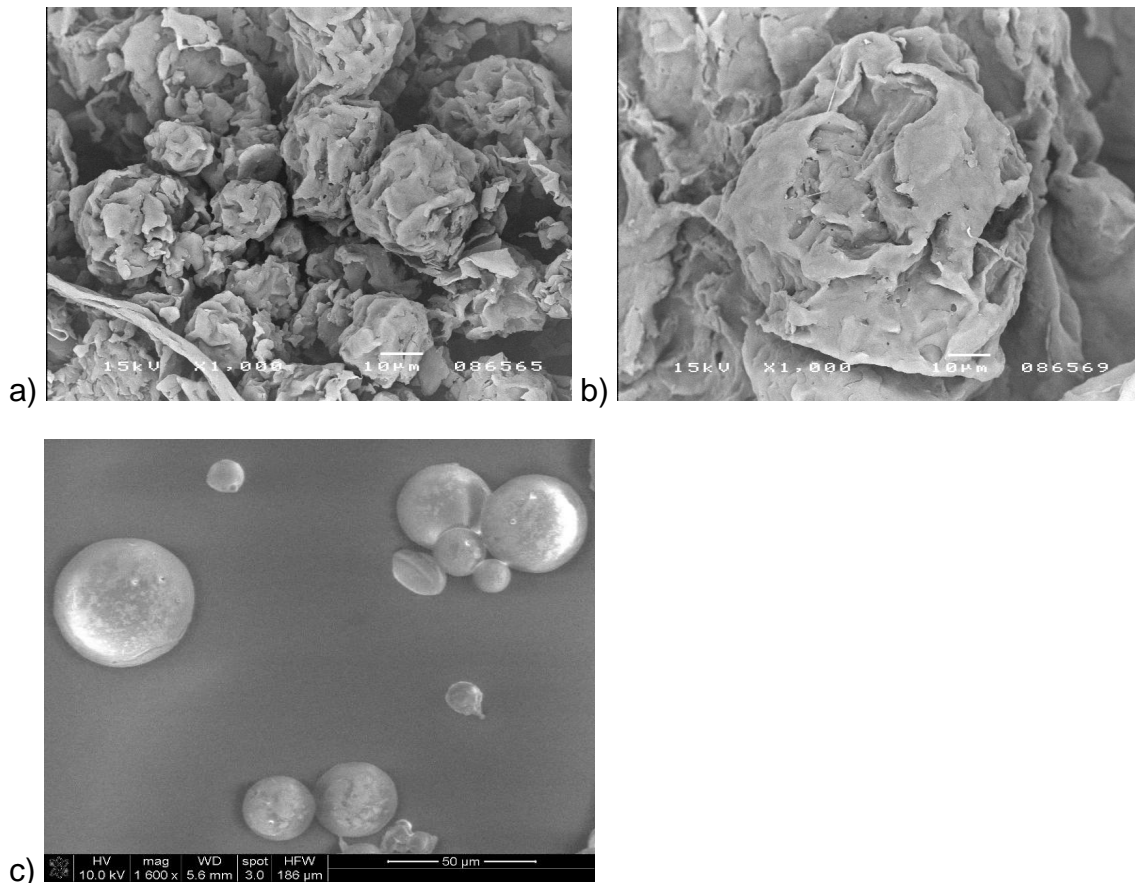
**Figure 3.** SEM images of the samples (a) COPLA 18, (b) COPLA 19 obtained with the participation of chloroform and methylene chloride, respectively



**Figure 4.** SEM image of samples: (a) BWEC5 prepared with chloroform as solvent and (b) BWEC6 prepared with ethyl acetate as solvent.

#### 5.1.4.4. The effect of the amount of polymer used and the type of solvent.

Bee wax is difficult to dissolve. It dissolves at elevated temperatures only in some organic solvents. If a polylactide is used as the shell material and a larger amount of bee wax as the core material, the obtained products have an uneven surface (Fig.5a,b). As can be seen, the use of ethyl acetate as a solvent allows microcapsules with a smoother surface to be obtained (Fig.5c). This was probably due to the better solubility of bee wax in ethyl acetate and the use of a smaller amount.

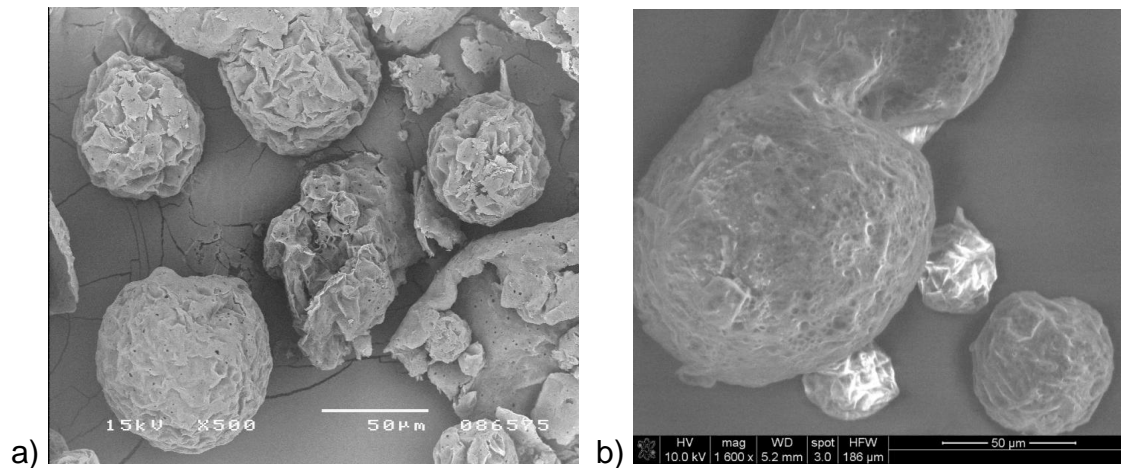


**Figure 5.** SEM images of bee wax microcapsules, in which BWPLA 1 (a) and BWPLA 4 (c) were made with the same solvent but in different proportion, and BWPLA3 (b) was made with a different solvent.



5.1.4.5. The effect of the amount of core material used.

As can be seen in Figure 6, the use of a smaller amount of core material allows microcapsules with a smoother surface.



**Figure 6.** SEM image of samples: (a) BWEC3 with 0.2g of bee wax as a core material, (b) BWEC4 with 0.1g of bee wax as a core material.

The average diameter of the developed microcapsules was calculated to be around 26  $\mu\text{m}$ . This indicates that the microcapsules are tiny and easy to coat onto the fabric surface. The results are summarized in Table. 3

**Table 3.** Transversal average dimension of microcapsules

Capsule Diameter			
Sample	Mean value ( $\mu\text{m}$ )	Minimum value ( $\mu\text{m}$ )	Maximum value ( $\mu\text{m}$ )
COEC3	15.98	6.55	37.97
COEC4	16.95	5.86	40.17
COPLA20	19.41	7.08	39.79
COPLA21	26.09	7.28	45.51
BWEC2	24.91	9.51	45.90
BWPLA2	27.47	9.56	47.58
BWPLA3	21.80	15.98	27.47
BWEC3	34.14	13.32	80.15
BWEC4	51.73	13.11	110.65
BWPLA4	25.44	9.98	76.40
BWEC5	24.94	6.32	76.44
BWEC6	24.62	5.55	52.84

#### 5.1.5. THERMAL PROPERTIES OF POLYLACTIDE AND ETHYL CELLULOSE MICROCAPSULES WITH COCONUT OIL AND BEE WAX.

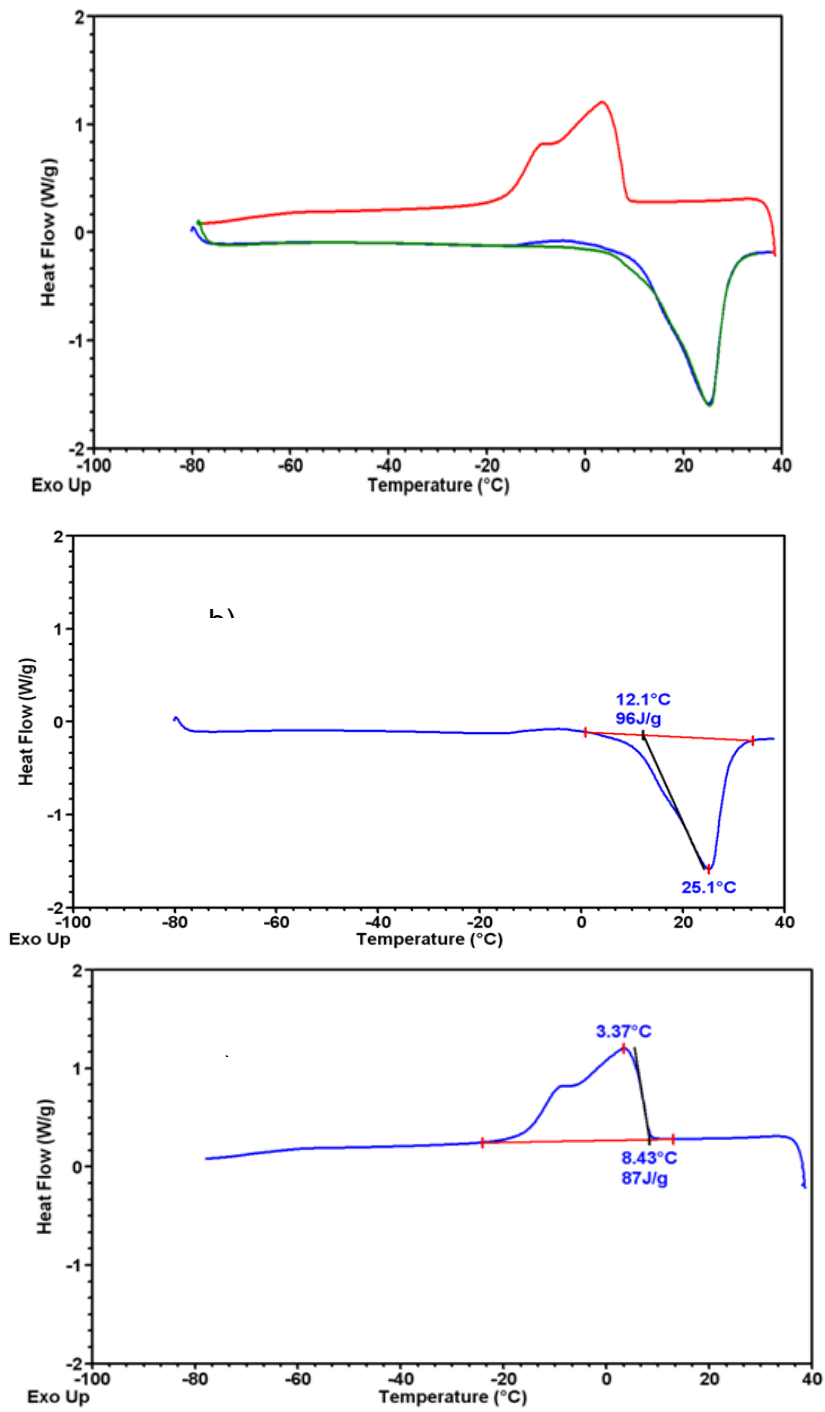
Poly lactide and ethyl cellulose microcapsules with coconut oil and bee wax were analyzed by DSC to compare their performances and operating temperatures for thermal energy storage.

The phase change latent heat of microcapsules can be determined by calculating the area under the endothermic peak. The encapsulate efficiency of microcapsules can be calculated by Equation (1):

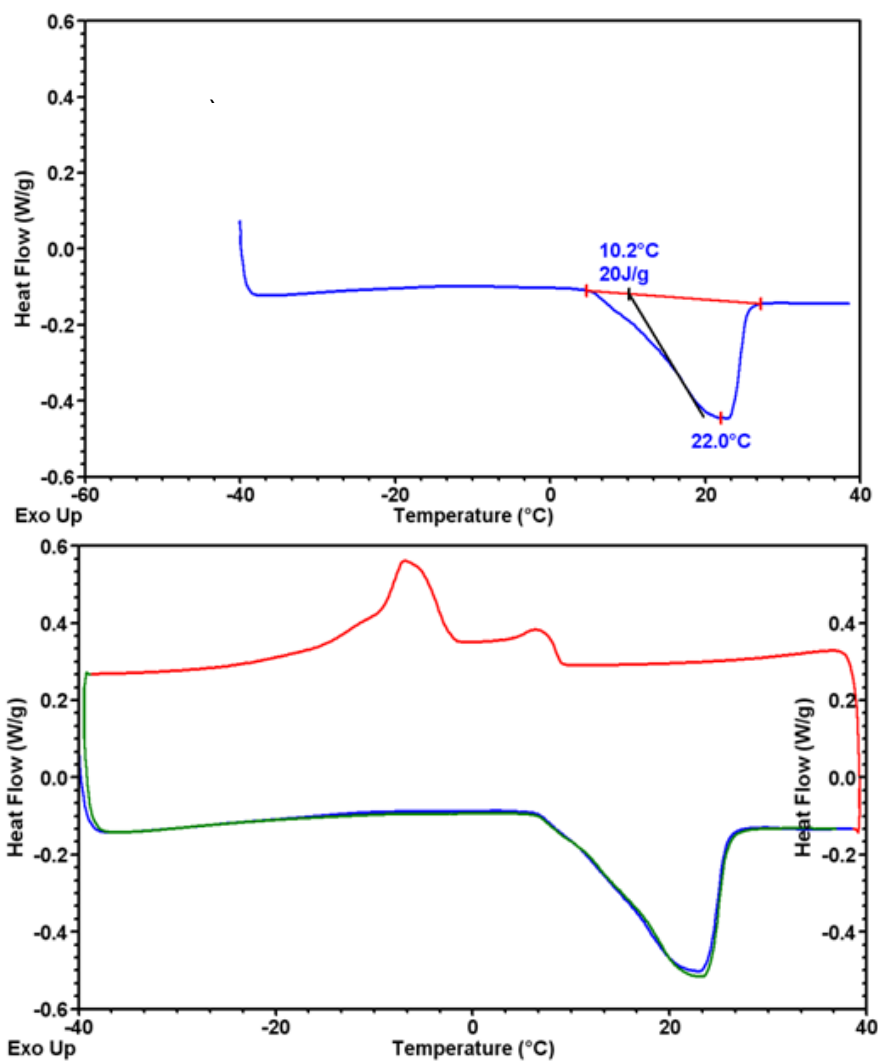
$$\text{Encapsulation efficiency} = \frac{\Delta H}{\Delta H_{PCM}} \times 100\% \quad (1)$$

where  $\Delta H$  and  $\Delta H_{PCM}$  are the latent heat of fusion of microcapsule and core material (coconut oil or bee wax), respectively.

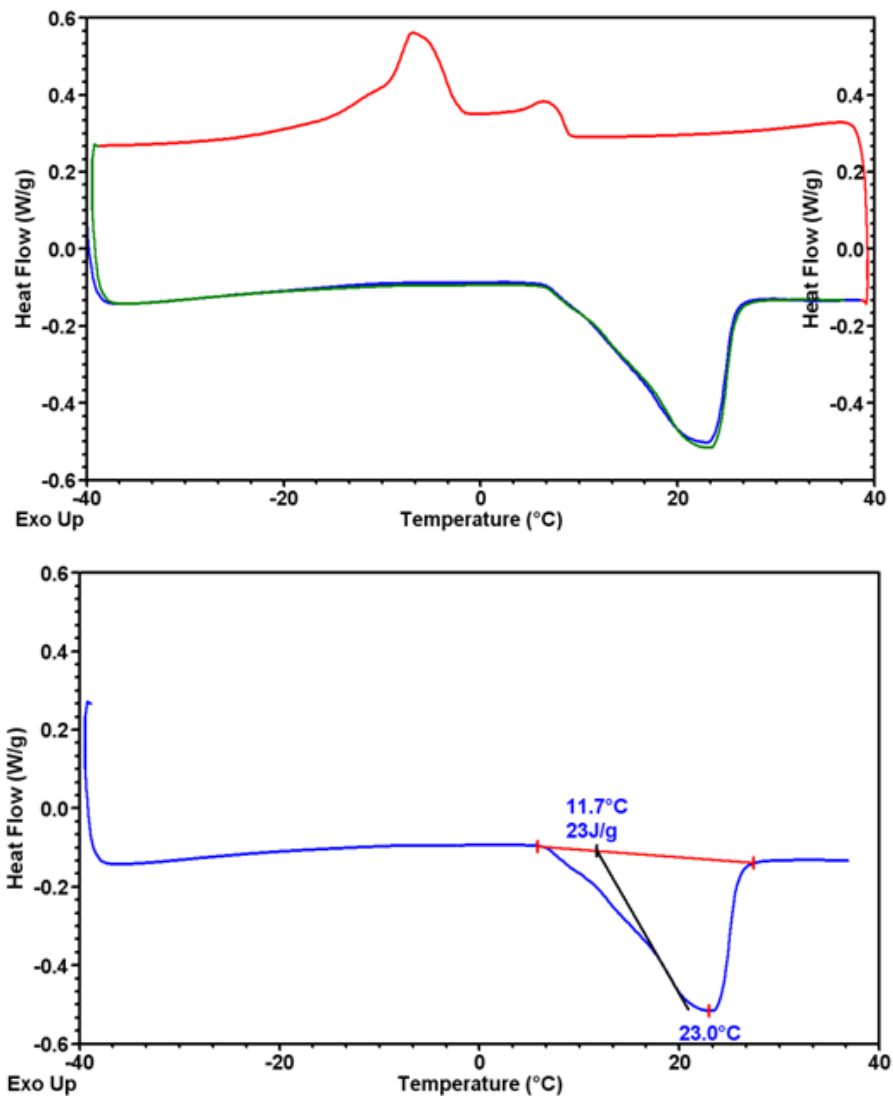
Figure 7-21 show DSC thermograms of coconut oil and bee wax and microcapsules containing these substances during heating and cooling cycles. Table 3 and 4 summarizes the encapsulate efficiencies of samples. The melting temperature of pure coconut oil is 25,1°C and in microcapsule form is about The melting temperature of pure bee wax is 55,9°C and in microcapsule form is about 57°C in all cases.



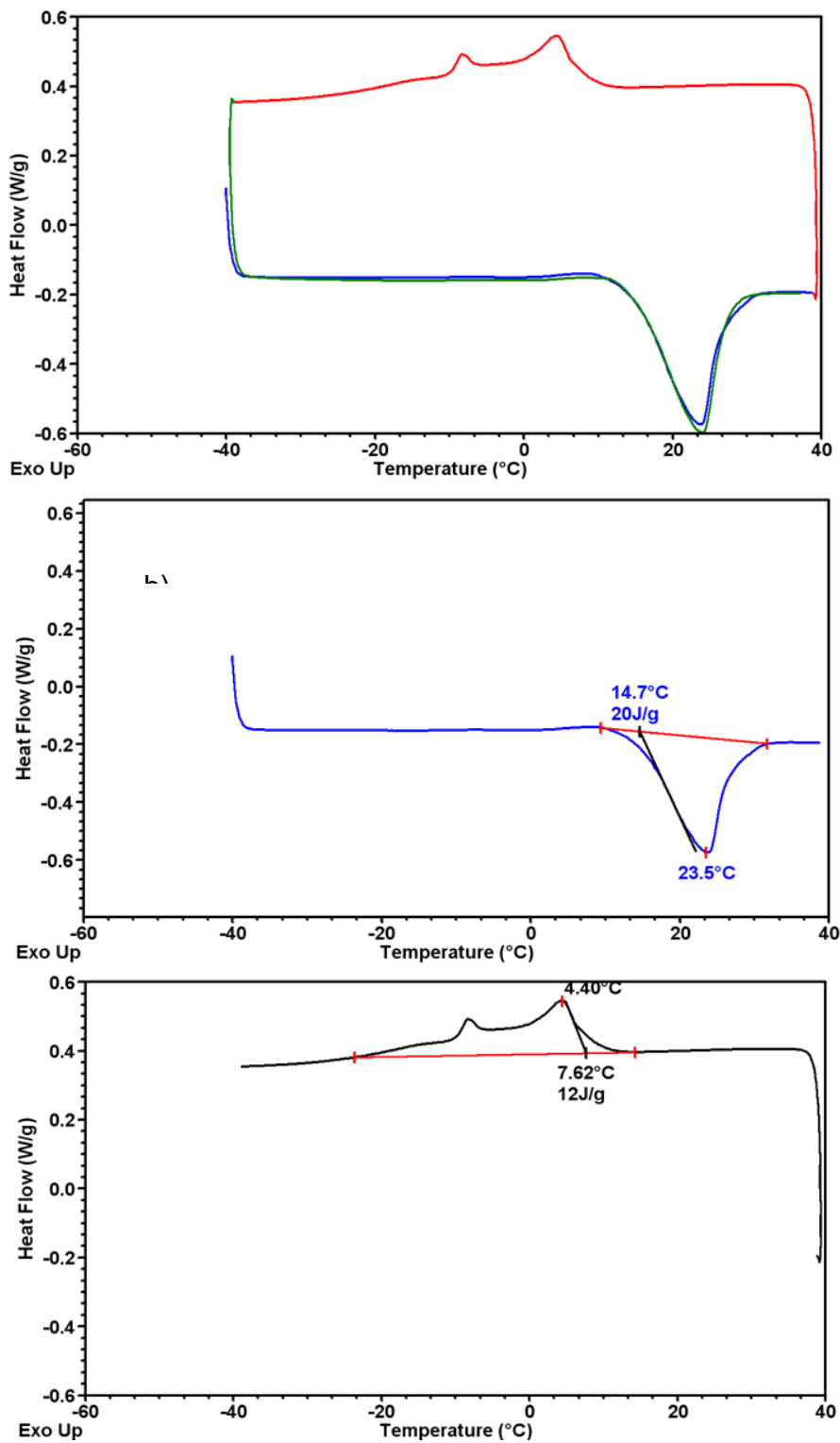
**Figure 7.** DSC thermograms of pure coconut oil: a) - complete cycle, b) - heating cycle, c) - cooling cycle



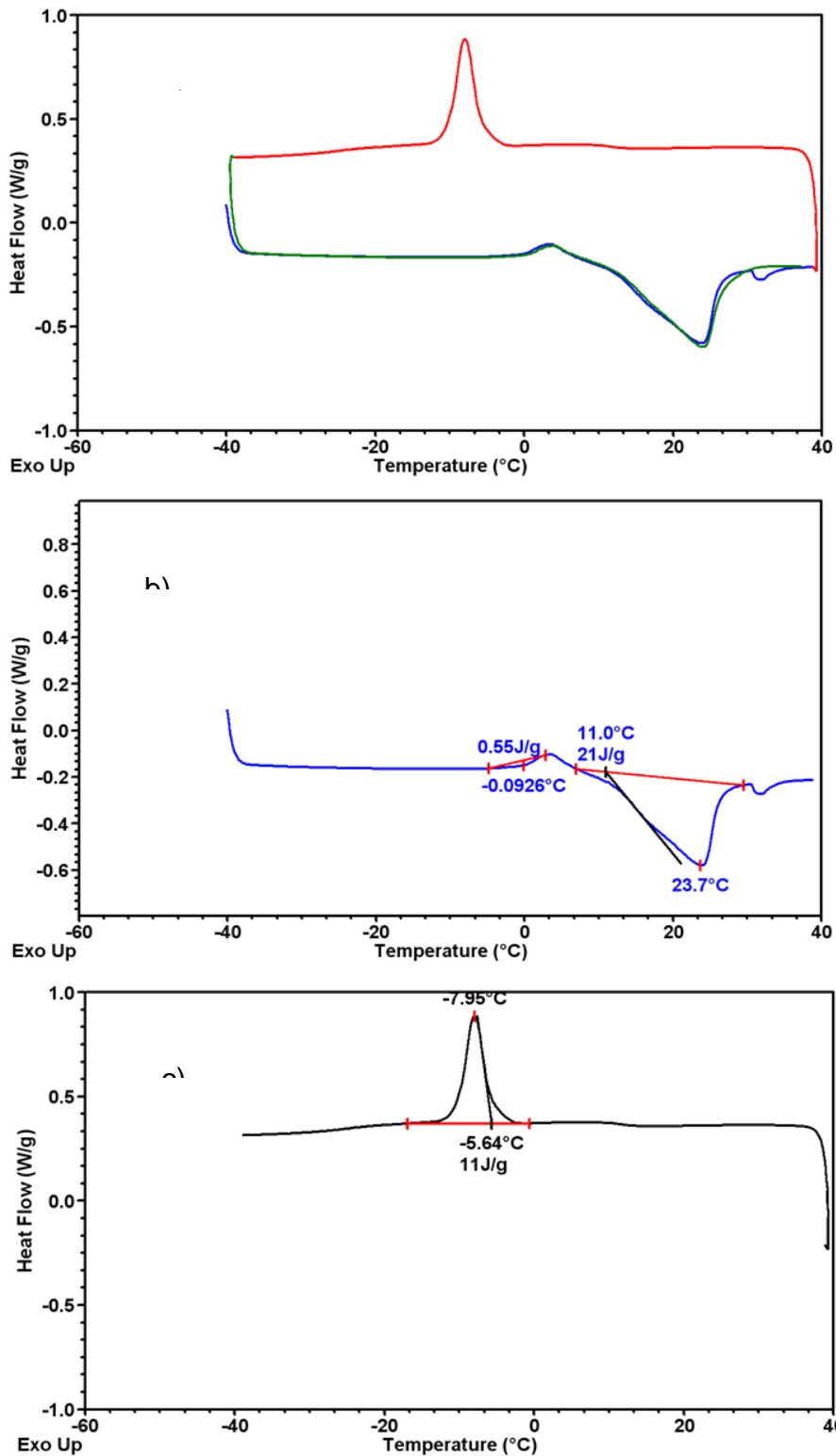
**Figure 8.** DSC thermograms of microcapsules COPLA6: a) - heating cycle, b) - complete cycle



**Figure 9.** DSC thermograms of microcapsules COPLA11: a) - complete cycle, b) - heating cycle

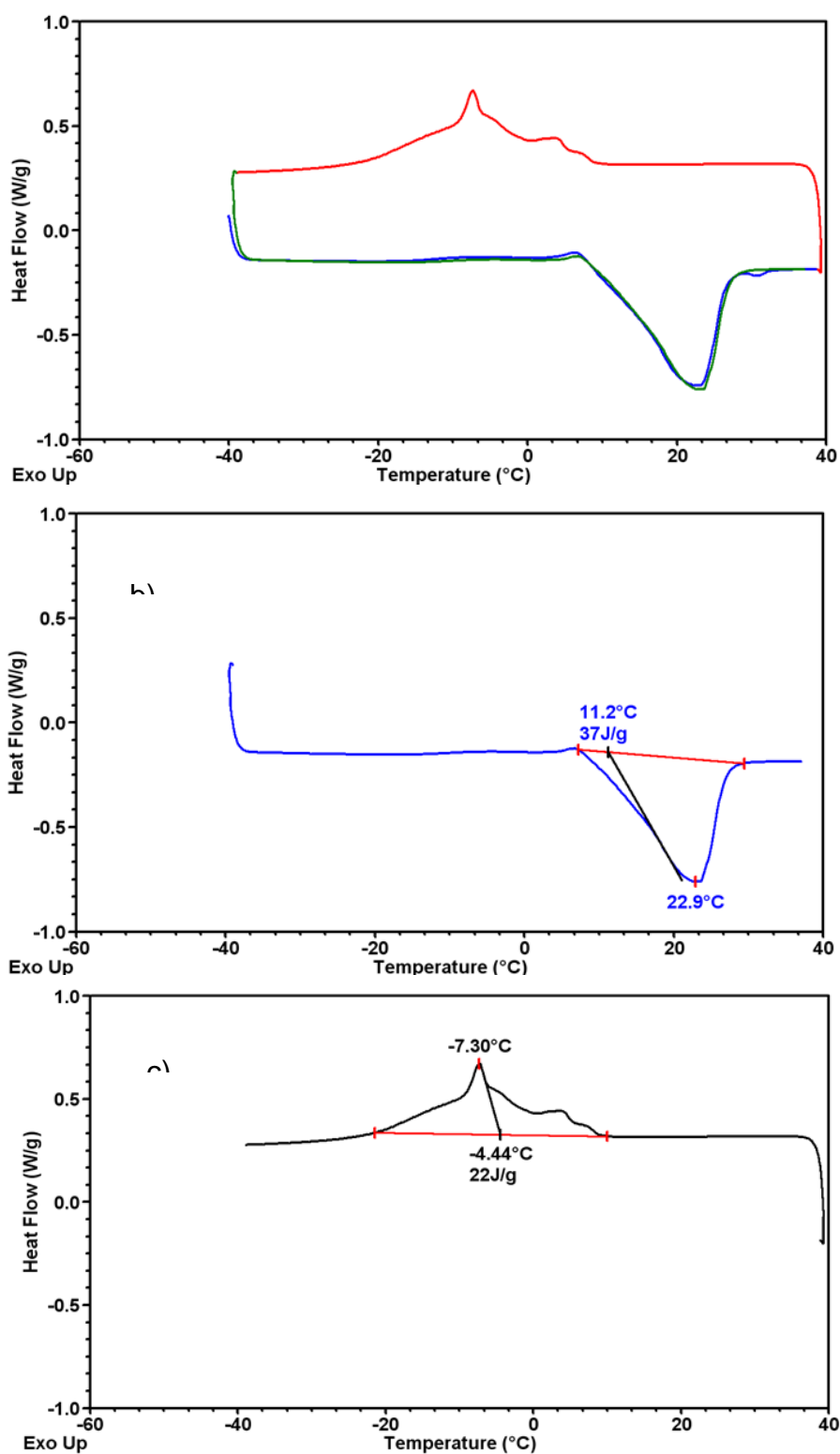


**Figure 10.** DSC thermograms of microcapsules COEC3: a) - complete cycle, b) - heating cycle, c) – cooling cycle

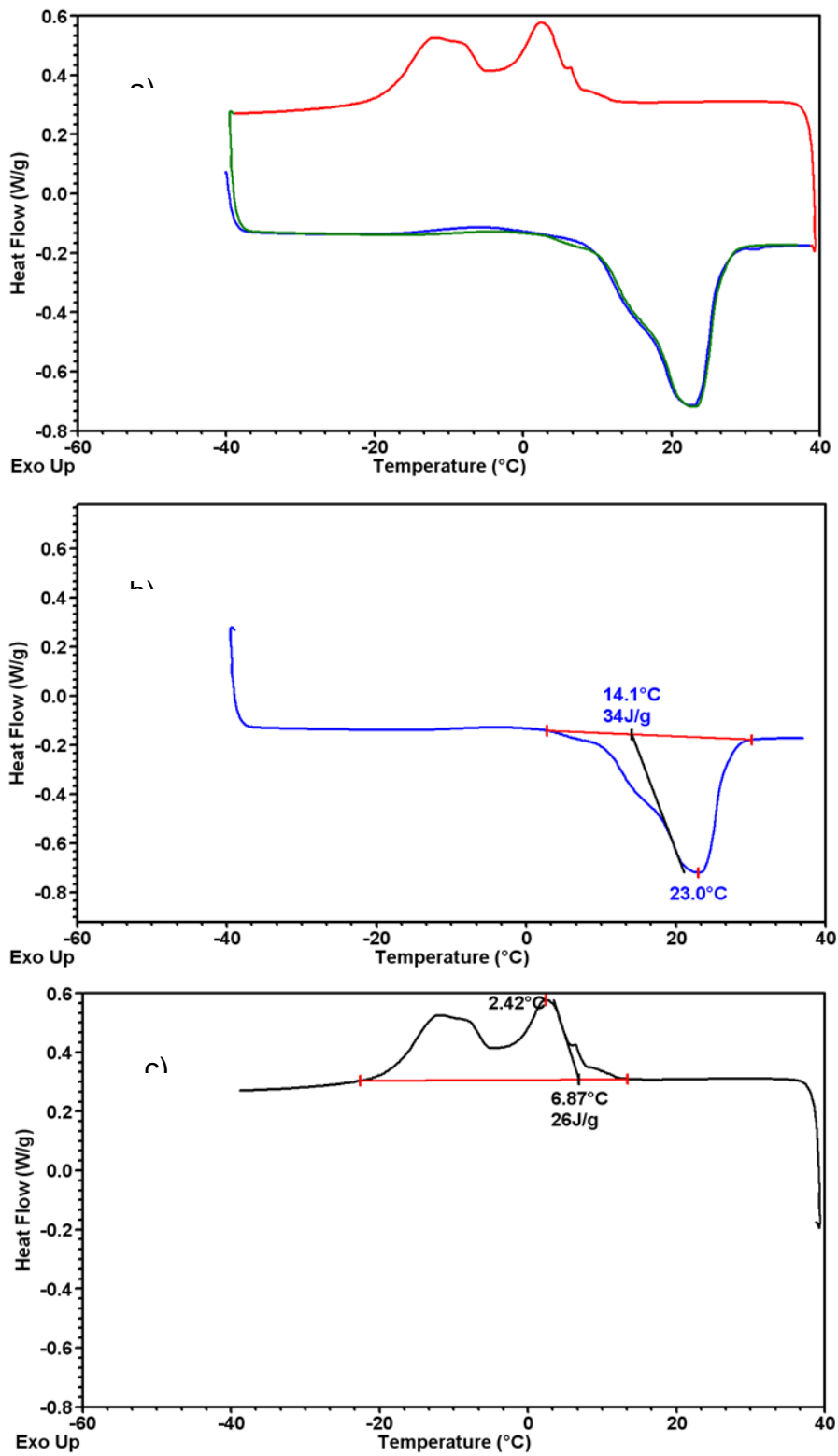


**Figure 11.** DSC thermograms of microcapsules COEC4: a) - complete cycle, b) - heating cycle, c) – cooling cycle

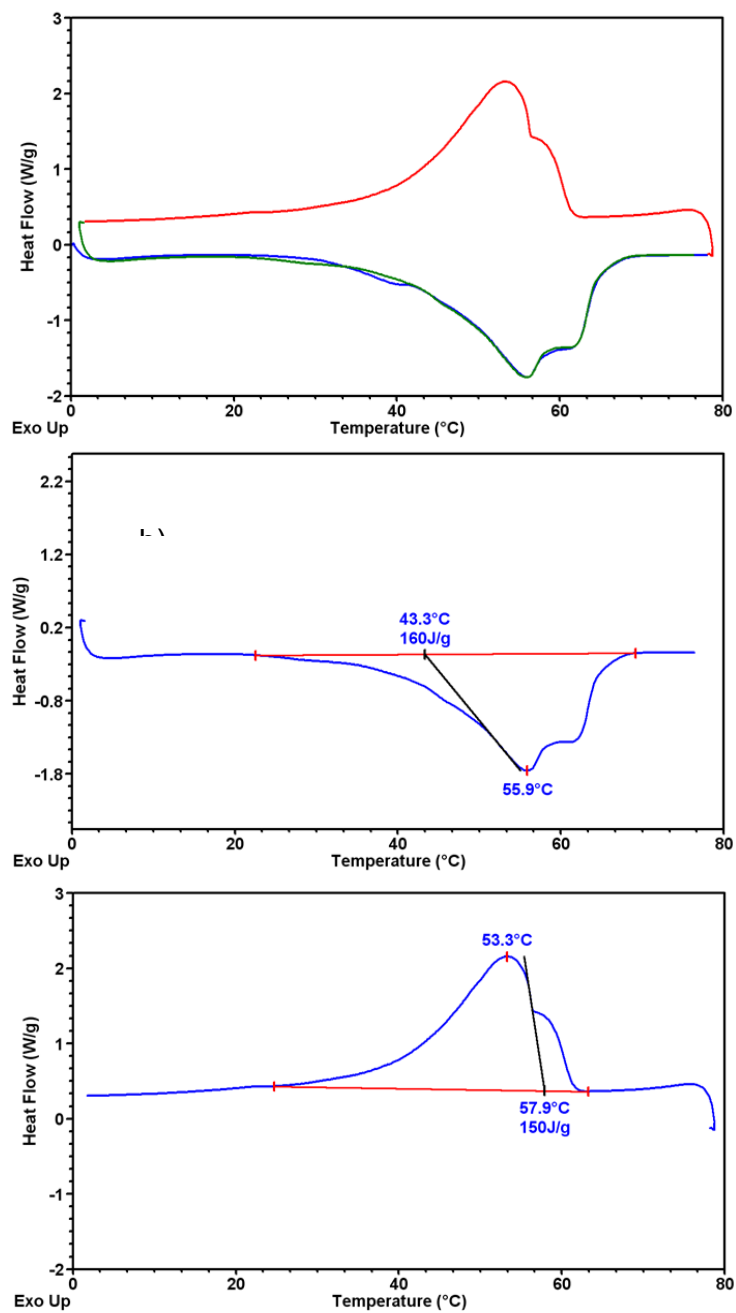




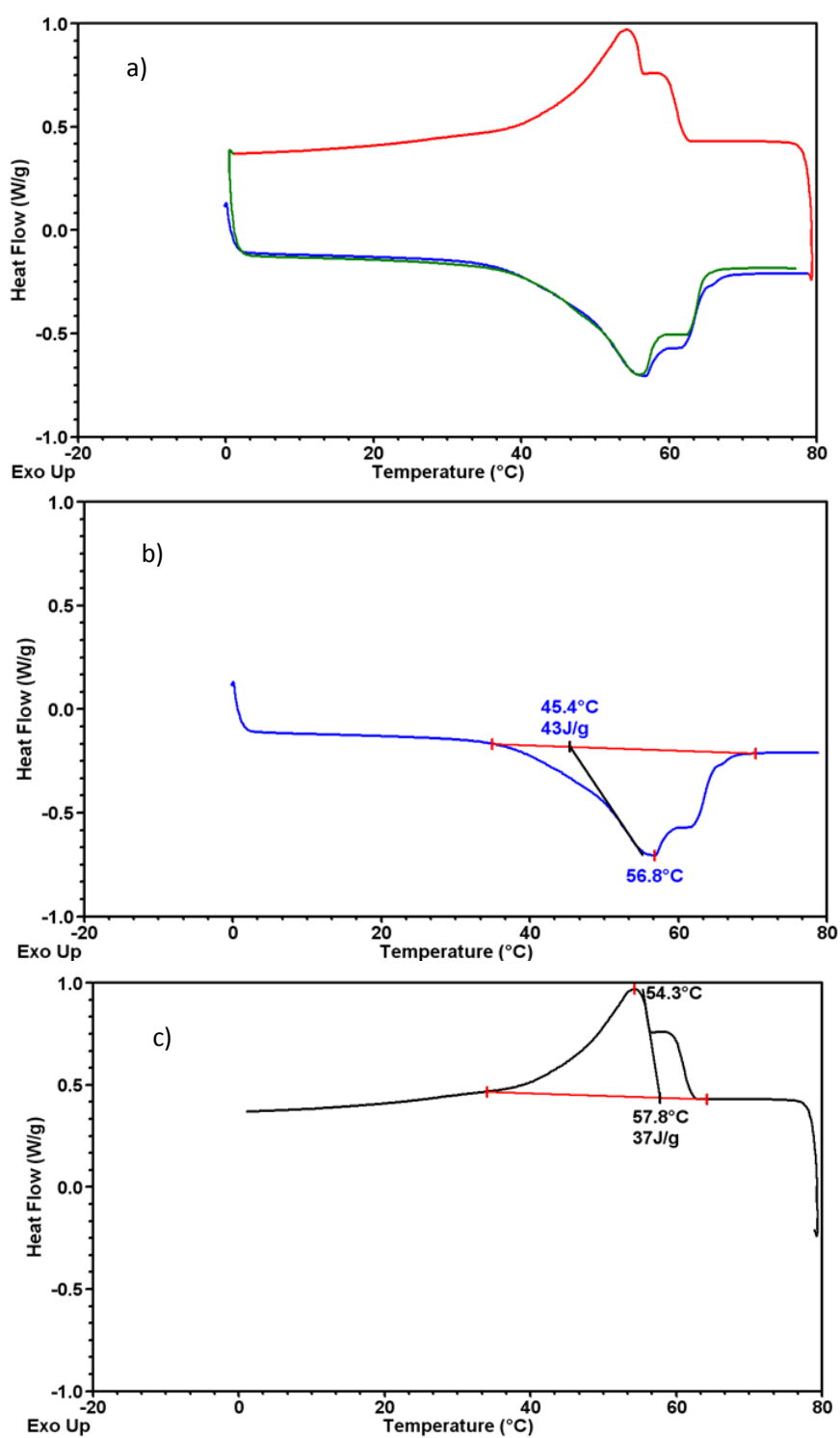
**Figure 12.** DSC thermograms of microcapsules COPLA20: a) - complete cycle, b) - heating cycle, c) – cooling cycle



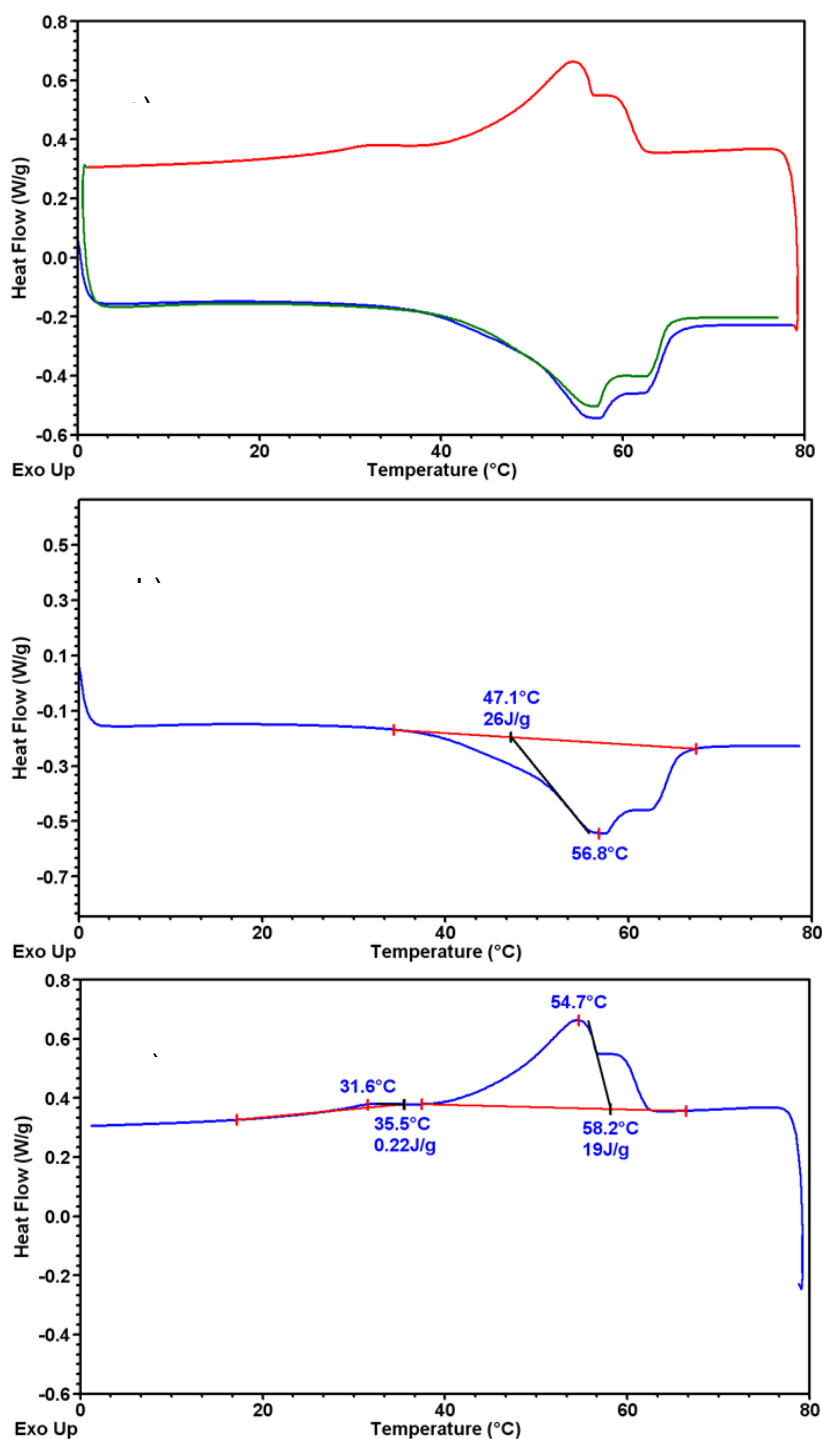
**Figure 13.** DSC thermograms of microcapsules COPLA21: a) - complete cycle, b) - heating cycle, c) – cooling cycle



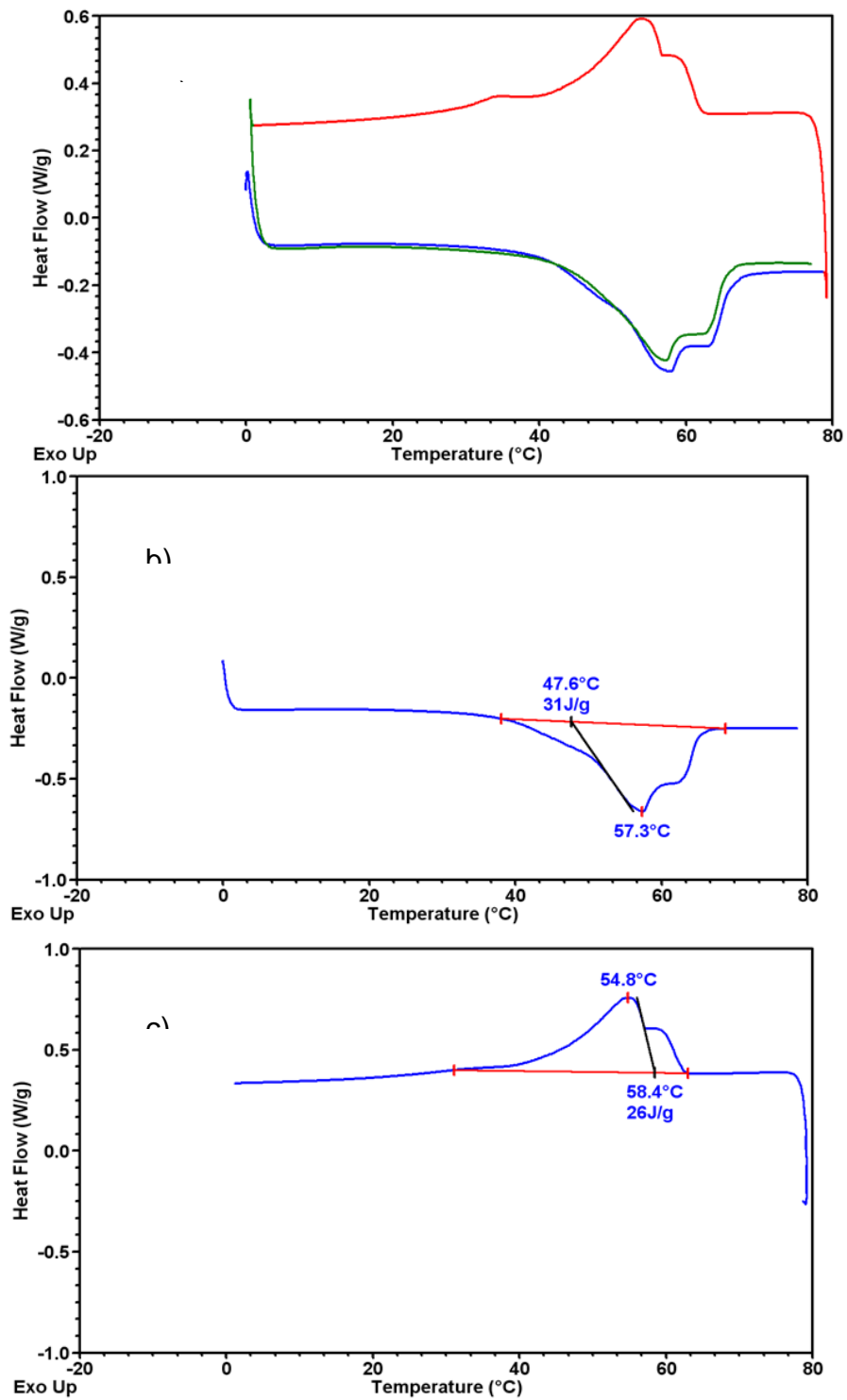
**Figure 14.** DSC thermograms of pure bee wax: a) - complete cycle, b) - heating cycle, c) – cooling cycle



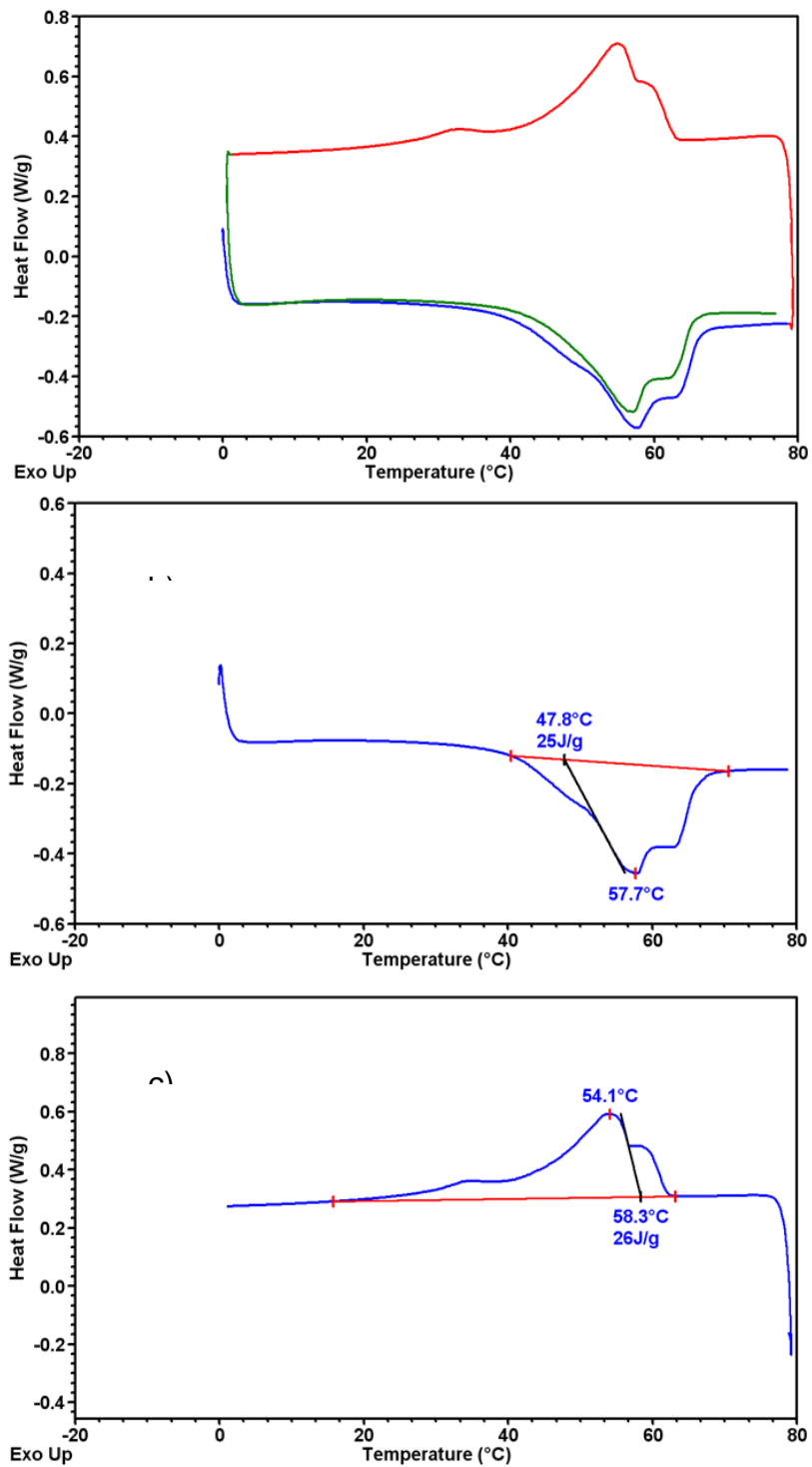
**Figure 15.** DSC thermograms of microcapsules BWEC3: a) - complete cycle, b) - heating cycle, c) – cooling cycle



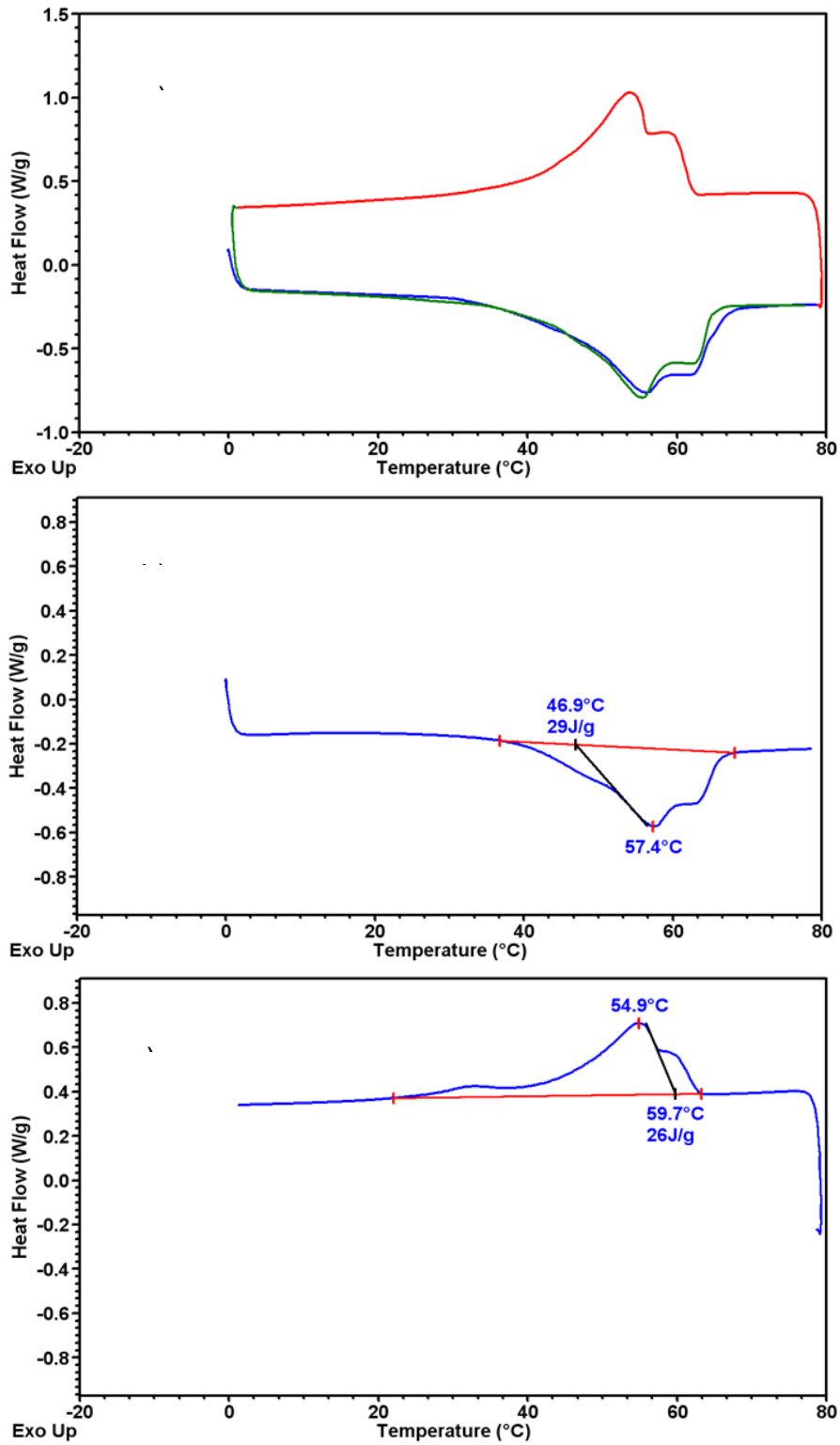
**Figure 16.** DSC thermograms of microcapsules BWEC4: a) - complete cycle, b) - heating cycle, c) – cooling cycle



**Figure 17.** DSC thermograms of microcapsules BWEC5: a) - complete cycle, b) - heating cycle, c) – cooling cycle

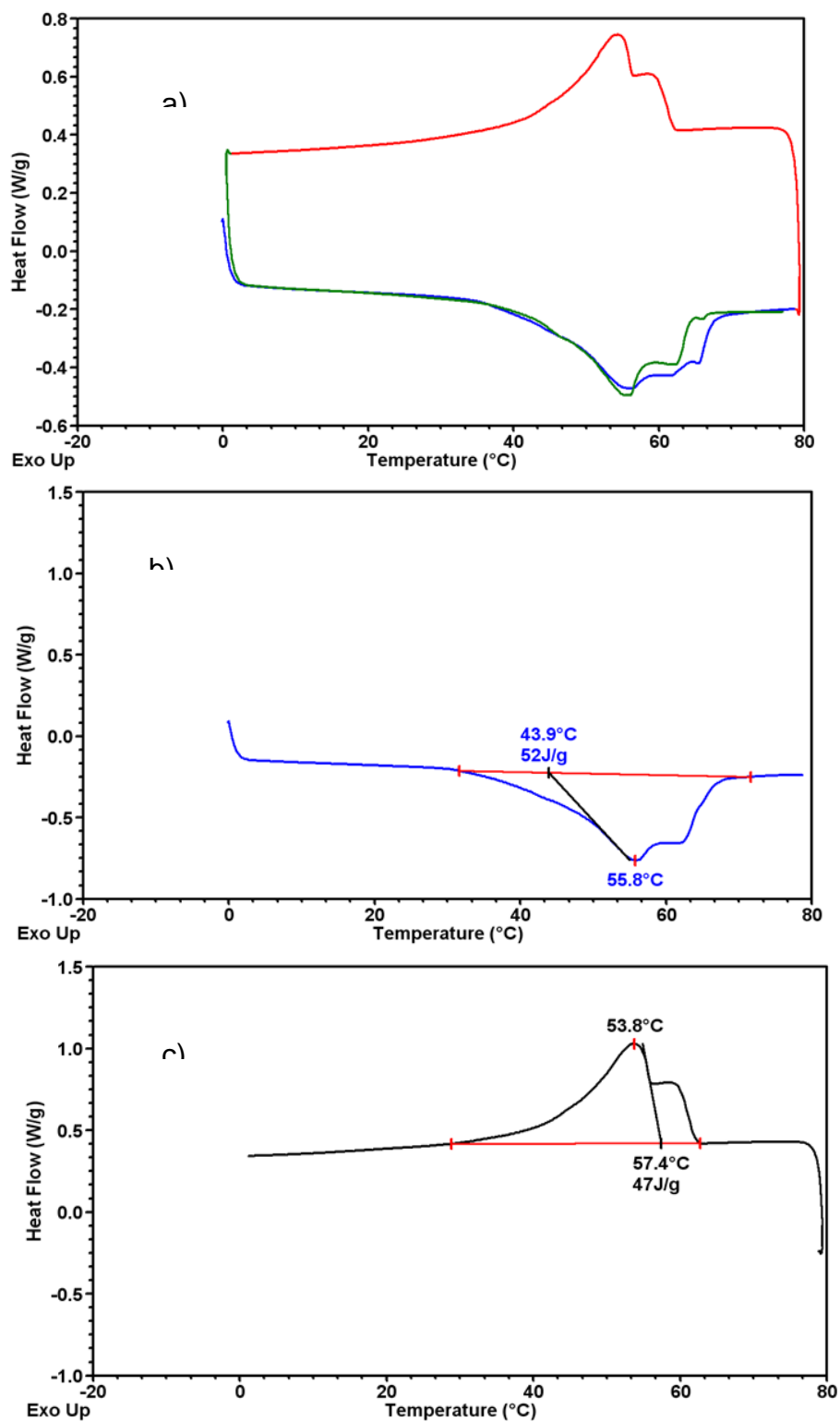


**Figure 18.** DSC thermograms of microcapsules BWEC6: a) - complete cycle, b) - heating cycle, c) – cooling cycle

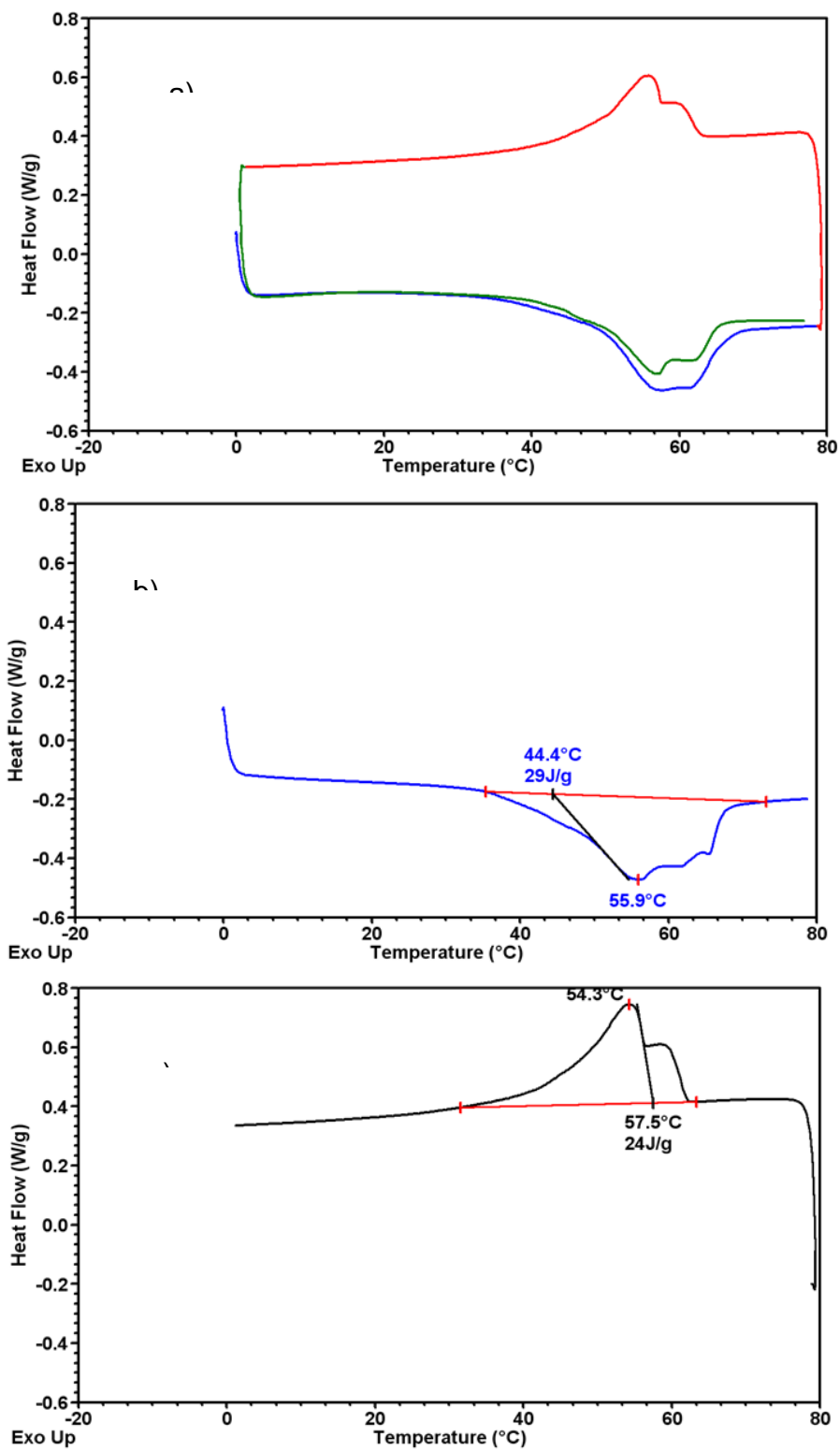


**Figure 19.** DSC thermograms of microcapsules BWPLA2: a) - complete cycle, b) - heating cycle, c) – cooling cycle





**Figure 20.** DSC thermograms of microcapsules BWPLA3: a) - complete cycle, b) - heating cycle, c) – cooling cycle



**Figure 21.** DSC thermograms of microcapsules BWPLA4: a) - complete cycle, b) - heating cycle, c) – cooling cycle

**Table 4.** Encapsulation efficiency of coconut oil.

SAMPLE	Latent heat of PCM (J/g)	Encapsulation Efficiency (%)
Coconut oil	96.0	-
COPLA6	20.00	20.83%
COPLA11	24.00	25.00%
COEC3	20.00	20.83%
COEC4	18.00	18.75%
COPLA20	37.00	38.54%
COPLA21	34.00	35.42%

**Table 5.** Encapsulation efficiency of bee wax.

SAMPLE	Latent heat of PCM (J/g)	Encapsulation Efficiency (%)
Bee wax	160.0	-
BWEC2	43.00	28.67%
BWPLA2	52.00	34.67%
BWPLA3	29.00	19.33%
BWEC3	26.00	17.33%
BWEC4	31.00	20.67%
BWPLA4	21.00	14.00%
BWEC5	25.00	16.67%
BWEC6	31.00	20.67%

The core content of coconut oil were calculated to be from 18.75 wt% to 38,42 wt%, depending on the type of polymer used and the process conditions . In the case of microcapsules with bee wax, a similar relationship can be observed.

The core content in microcapsules were calculated to be from 14.0 wt% to 34,67 wt%.

#### 5.1.6. MODIFICATION OF TEXTILES WITH MICROENCAPSULATED PHASE CHANGE MATERIAL.

The modification of textiles is carried out due to the need to provide a new property to the textile fabric or to improve one that already has. In this case, it is intended to modify the textile by introducing microcapsules inside it. Below is the procedure of the experiments made and the tests done to observe how they work.

##### 5.1.6.1. Textile preparation with Microcapsules.

In order to keep microcapsules inside the fabric it was used two different binder; Sodium Alginate and Chitosan.

For modification of the textiles a nonwoven PLA sample of 8 x 6 centimeters was cut. The nonwoven samples were sprayed with 3% sodium alginate solution water used as a binder. The microcapsules were deposited with the use of a powder sprayer onto the surface prepared in this way. The product was then sprayed with sodium alginate solution again and lyophilized. The binder was transformed into a product insoluble in water by immersing the material in 10% calcium chloride solution.

In the case of using chitosan as a binder, the process proceeds as above except for the coagulation process.

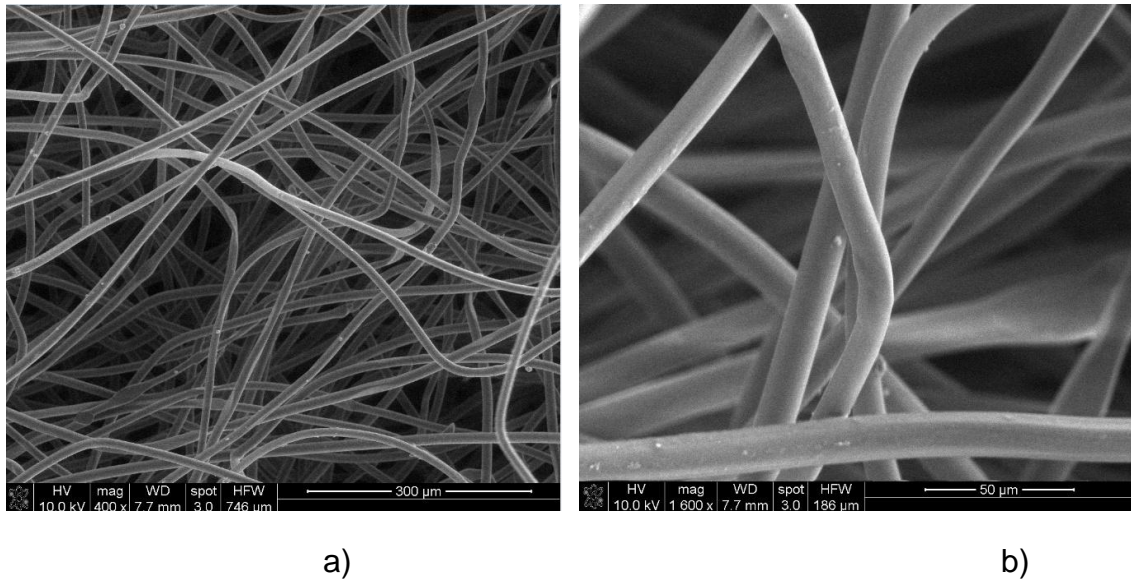
##### 5.1.6.2. Characterization of modified textiles by Scanning Electron Microscope (SEM).

Once the textiles have been modified, it is necessary to corroborate that they actually have microcapsules inside them and the easiest and most viable way is the observation of the textiles in the scanning electron microscope (SEM). Therefore, the images obtained from the modified textiles are shown below.

As can see in Figure 23-28 the application of calcium alginate and chitosan enabled effective distribution of microcapsules on the surface of the PLA nonwoven.

### Non-woven PLA textile without modification.

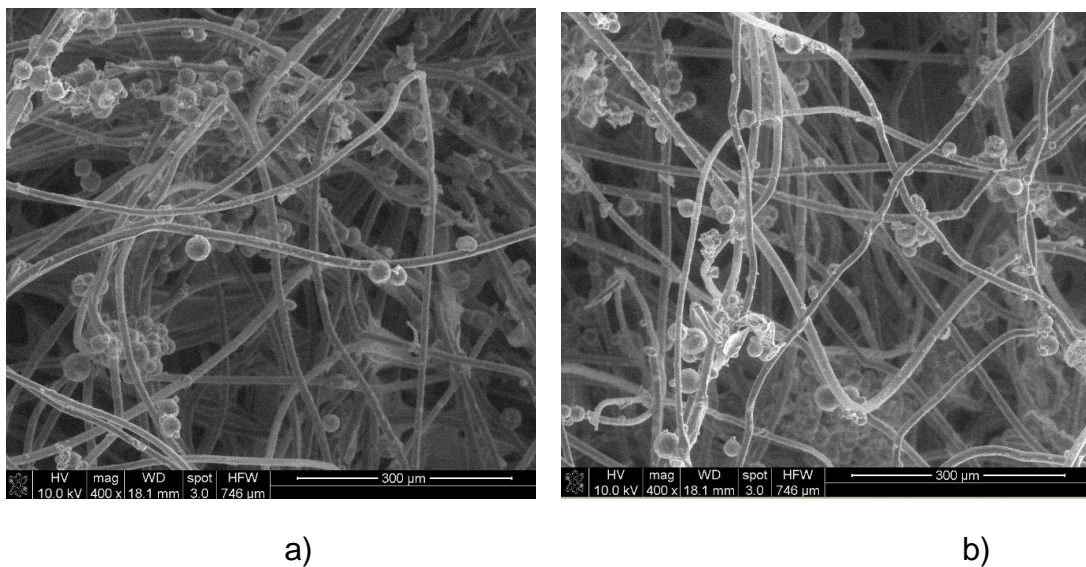
In order to compare the nonwoven PLA textile before and after microcapsules application this images above (figure 22) were taken from the SEM.



**Figure 22.** SEM images of non-woven PLA (a) at 400x magnification and (b) 1600x magnification.

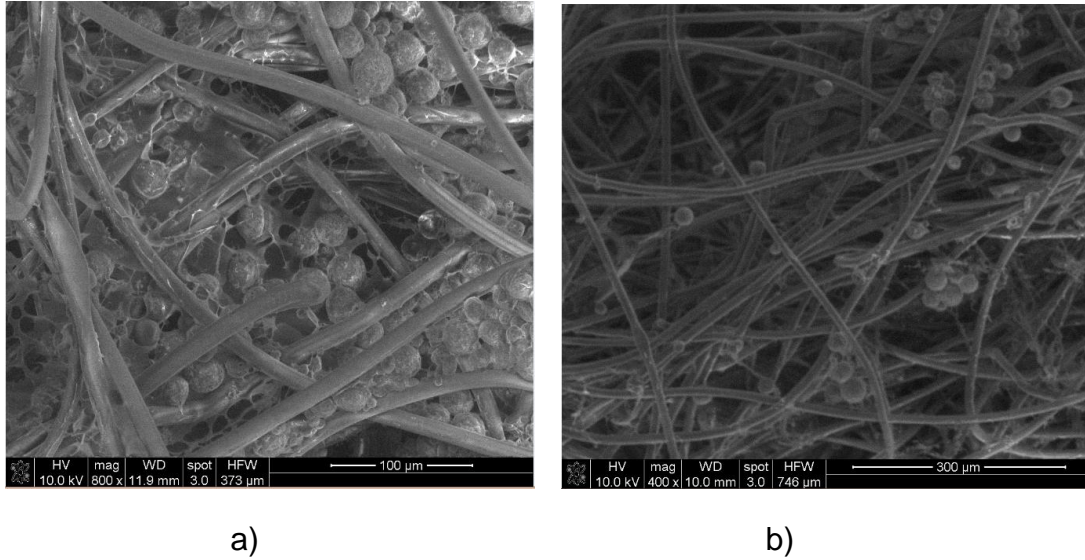
### 5.1.7. MODIFIED TEXTILES WITH COCONUT OIL MICROCAPSULES.

#### NON-WOVEN PLA WITH COEC3 AND SODIUM ALGINATE



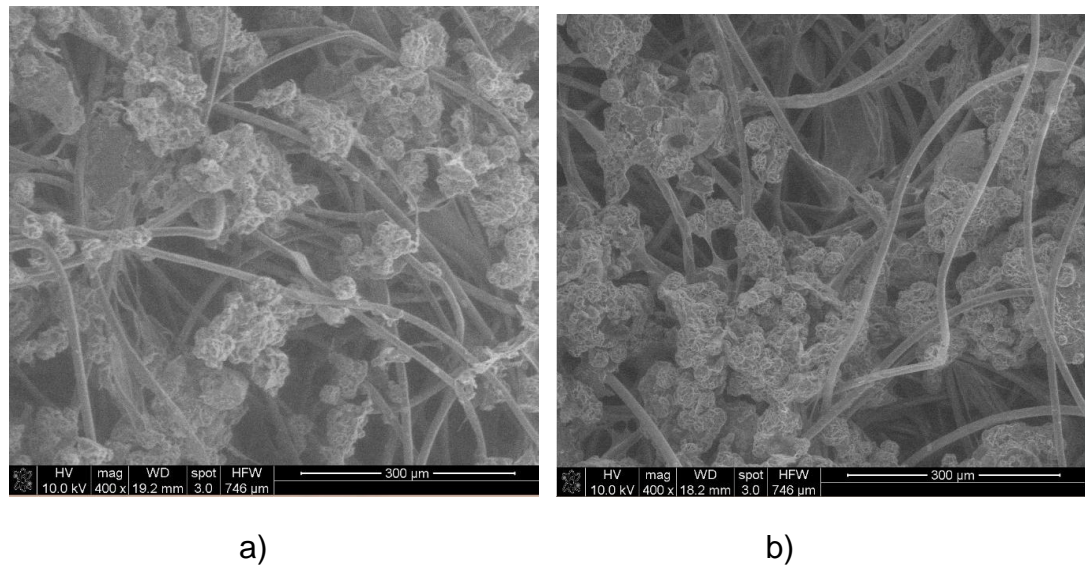
**Figure 23.** Non-woven PLA SEM images (a) and (b) with microcapsules COEC3 inside stuck them with Sodium Alginate.

## NON-WOVEN PLA WITH COEC3 AND CHITOSAN



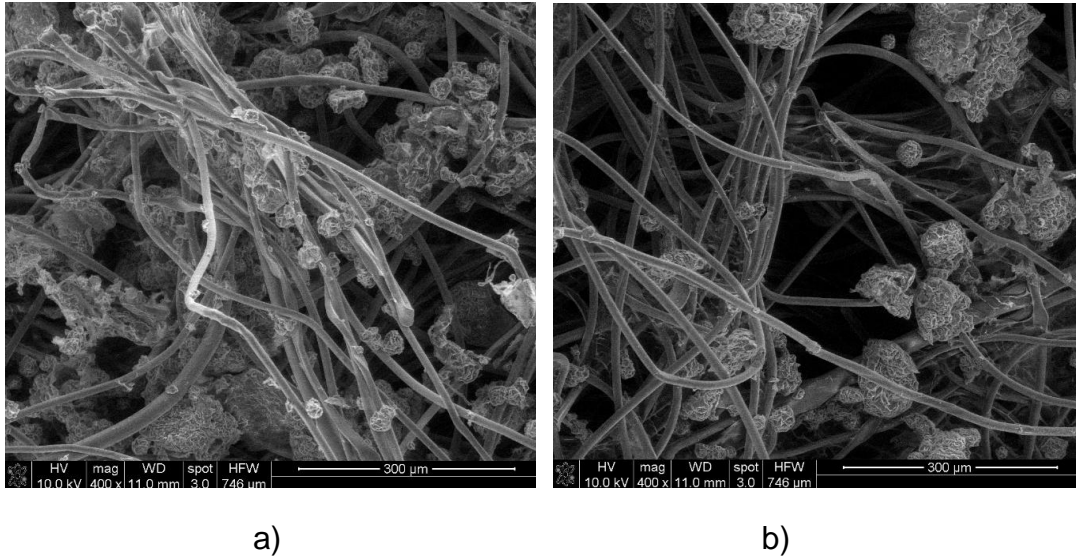
**Figure 24.** SEM images (a) and (b) with microcapsules COEC3 inside stuck them with Chitosan.

## NON-WOVEN PLA WITH BWEC2 AND SODIUM ALGINATE



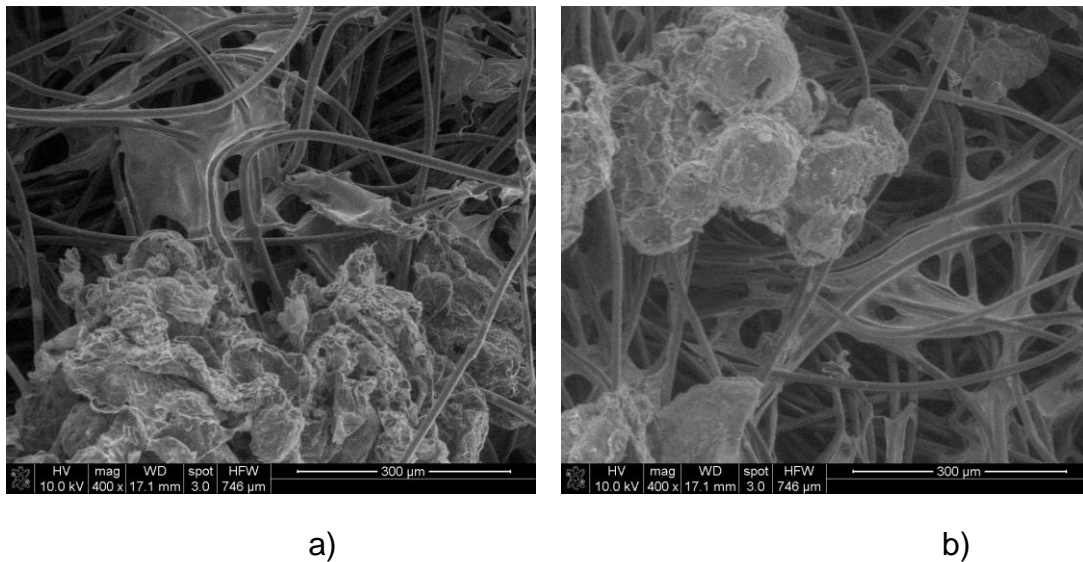
**Figure 25.** SEM images (a) and (b) of non-woven PLA with microcapsules BWEC2 inside stuck them with Sodium Alginate.

**NON-WOVEN PLA WITH BWEC2 AND CHITOSAN.**



**Figure 26.** SEM images (a) and (b) of non-woven PLA with microcapsules BWEC2 inside stuck them with Chitosan.

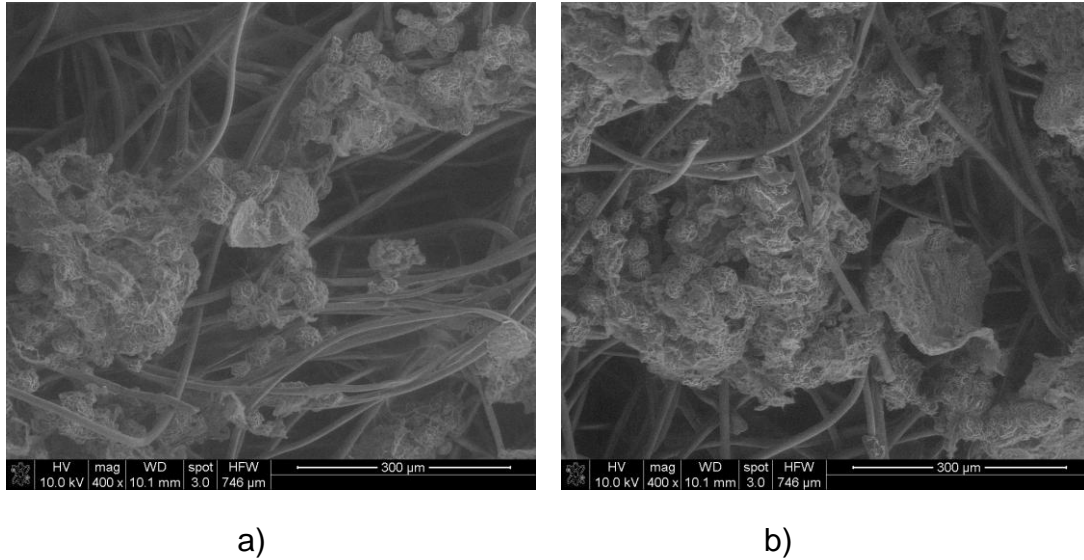
**NON-WOVEN PLA WITH BWPLA2 AND SODIUM ALGinate.**



**Figure 27.** Non-woven PLA SEM images (a) and (b) with microcapsules BWPLA2 inside stuck them with Sodium Alginate.



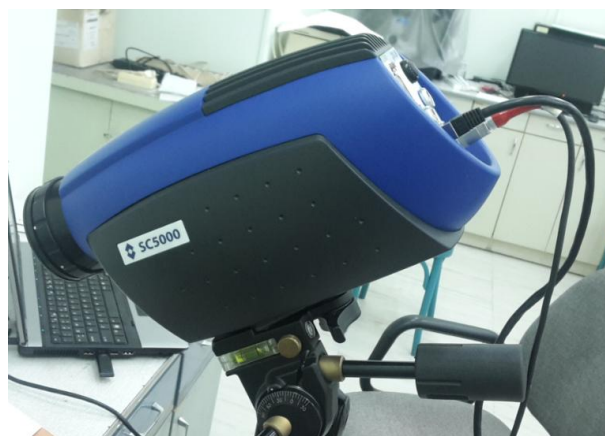
## NON-WOVEN PLA WITH BWPLA2 AND CHITOSAN.



**Figure 28.** Non-woven PLA SEM images (a) and (b) with microcapsules BWPLA2 inside stuck them with Chitosan.

### 5.1.8. INFRARED THERMOGRAPHY OF MODIFIED PLA NONWOVEN.

The thermal regulating properties were investigated by an IR camera (Figure 29). Samples (unmodified and modified) were placed on a hot plate (70°C) for 5 minutes. The pictures of samples were obtained after 0s, 50s and 100s after removal from the hot plate. The colours in the IR thermography images represent different temperatures.



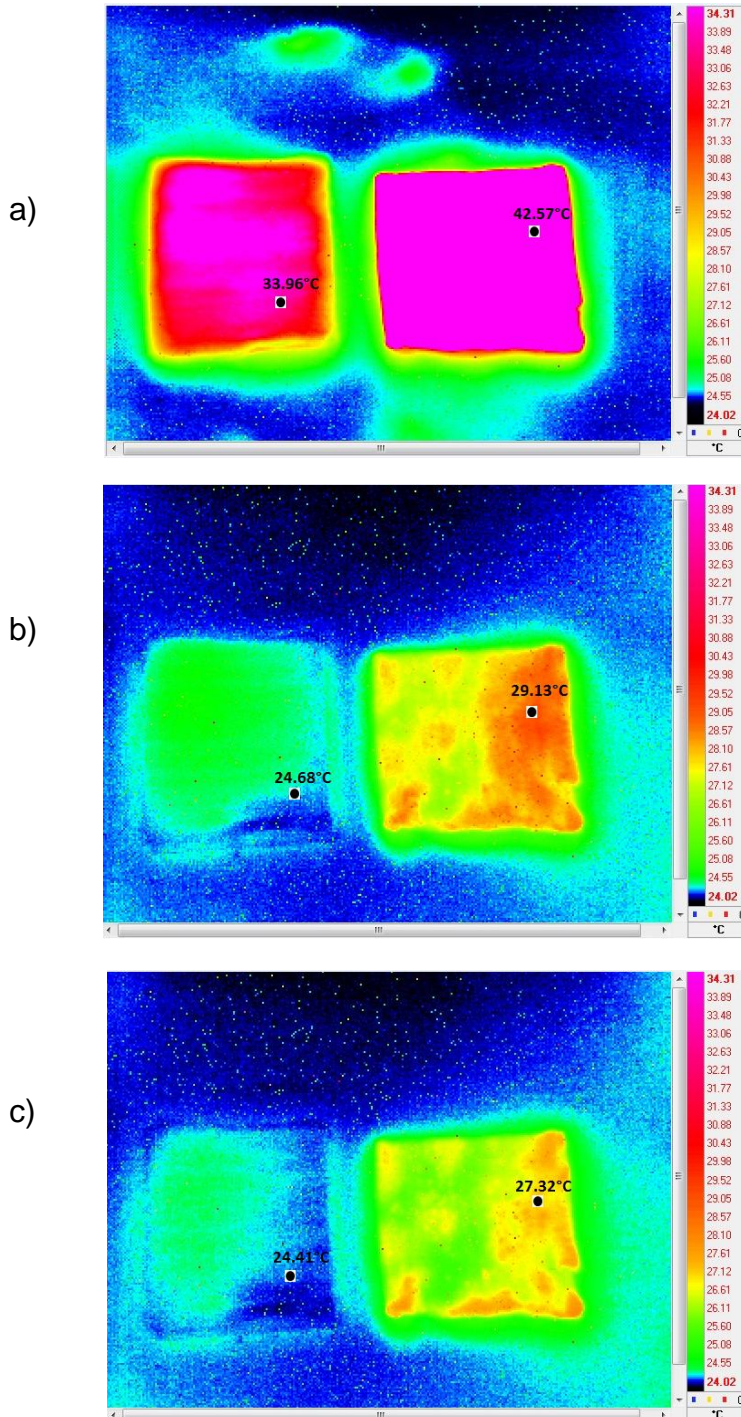
**Figure 29.** IR camera used for the testes

When comparing the thermal images in Figure 29-68 of modified samples and the unmodified sample, one can state that there is a difference between the reference sample and the samples coated with microcapsules with coconut oil or bee wax.

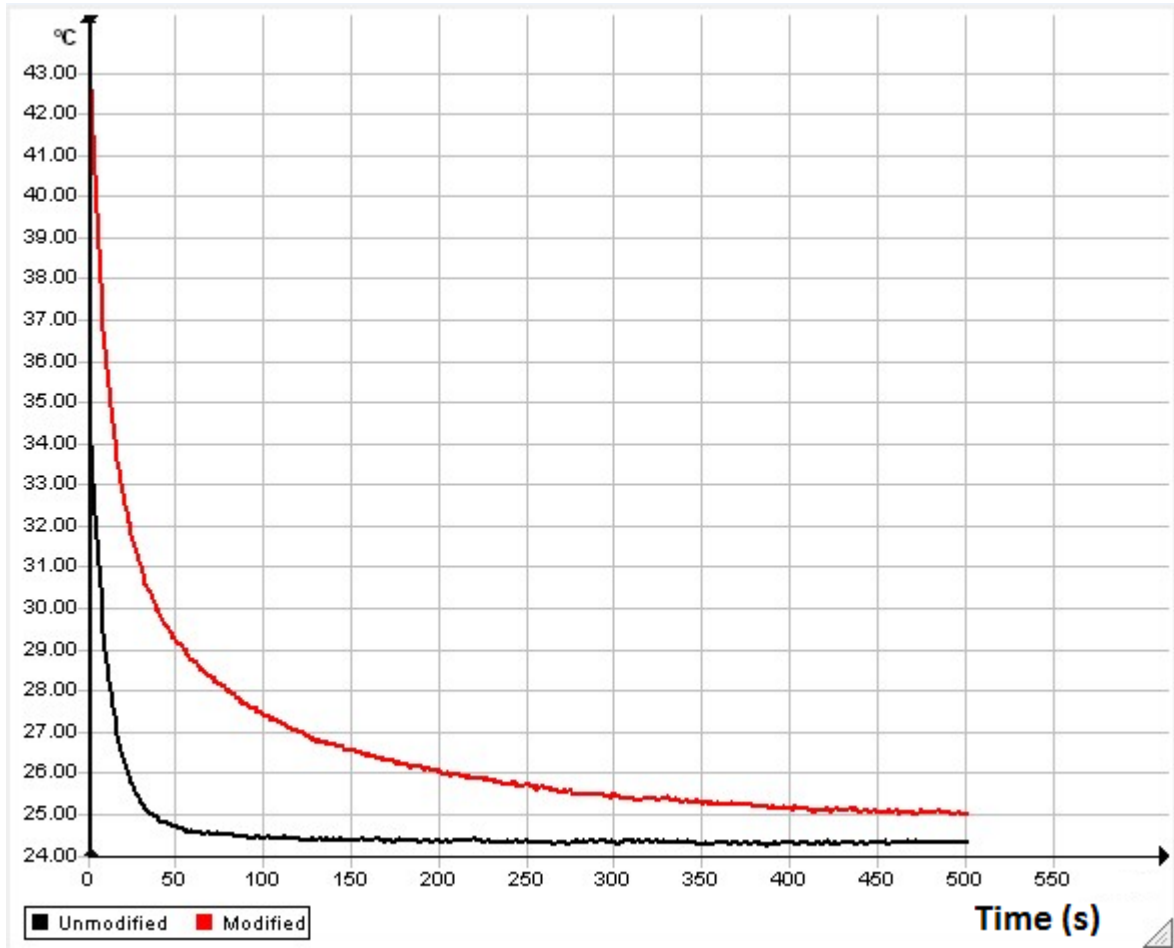
From the obtained images it can be concluded that the nonwoven regions containing PCM microcapsules undergo a slower cooling process than the reference sample. Although the difference is small, the change is sufficiently visible. This is most likely caused by thermoregulatory properties of coconut oil or beeswax microcapsules. It can also be seen that the cooling process of areas without microcapsules is also slower than the reference samples. It is probable that PCM absorbs heat during melting the phase change process, and thus absorbs heat from the rest of the material. It is also noted that there is no temperature increase with respect to the PCM containing part, because the PCM material is isothermal. The obtained graphs of temperature changes of the sample over time confirm the observed phenomenon on IR photos that the temperature of the unmodified sample decreases faster than the modified sample, which means that the modified sample can absorb more thermal energy and stay in it for a longer time due to microencapsulated material changes the phase that's inside. Modified nonwovens with microcapsules containing coconut oil or beeswax provide cooling effect, which confirms the effectiveness of the modification.

5.1.8.1. Modification of textiles with Coconut Oil microcapsules.

**COEC3 WITH SODIUM ALGINATE**

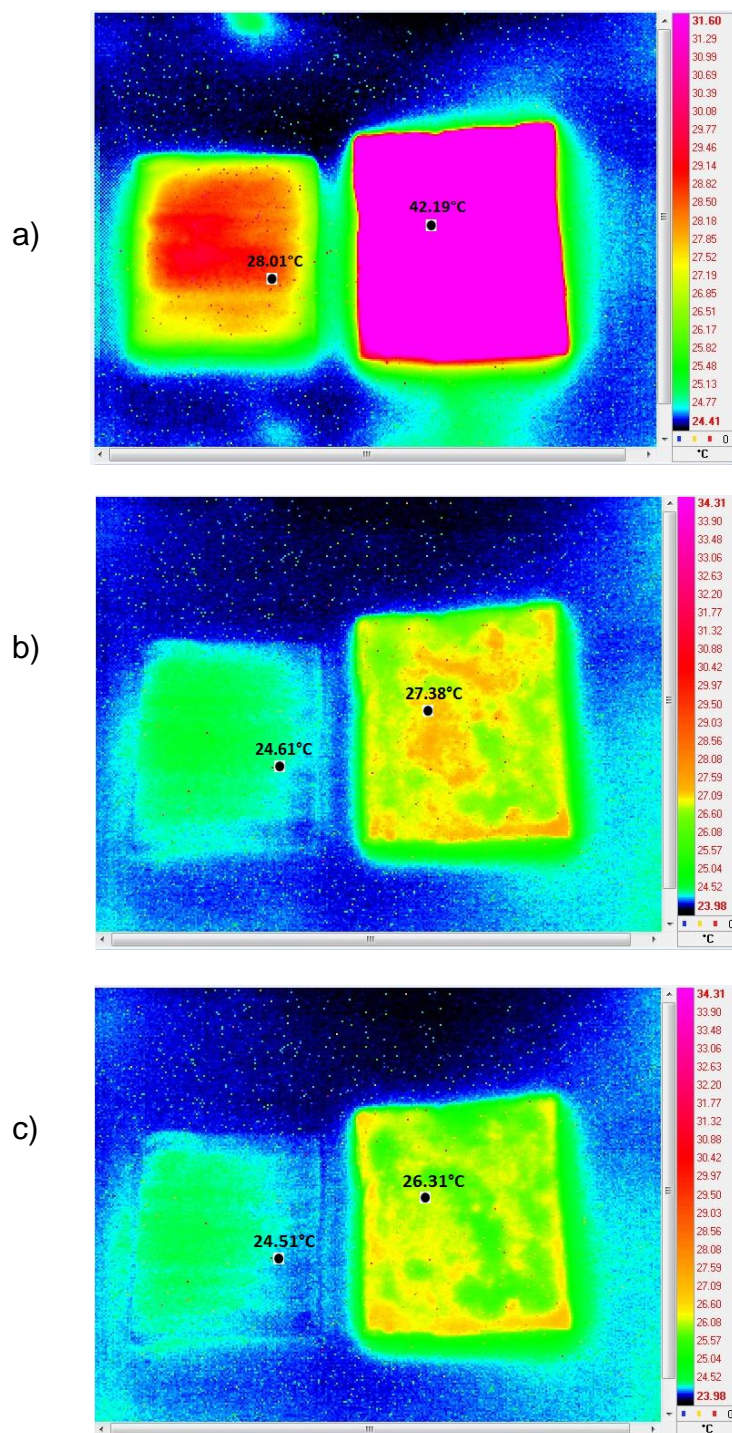


**Figure 29.** IR images of non-woven PLA unmodified (sample on the left) and modified with COEC3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

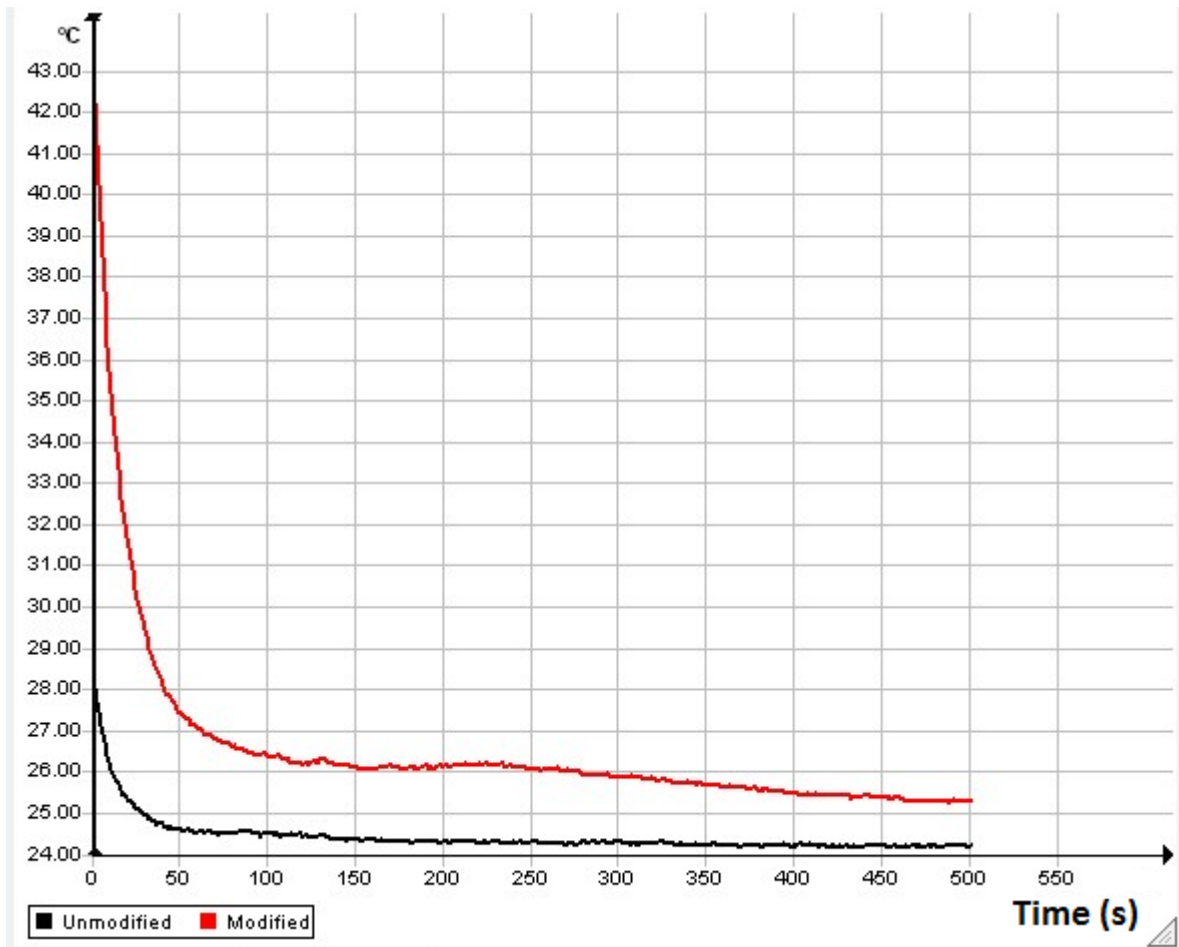


**Figure 30.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COEC3 microcapsules and sodium alginate as binder.

## COPLA20 WITH SODIUM ALGINATE.

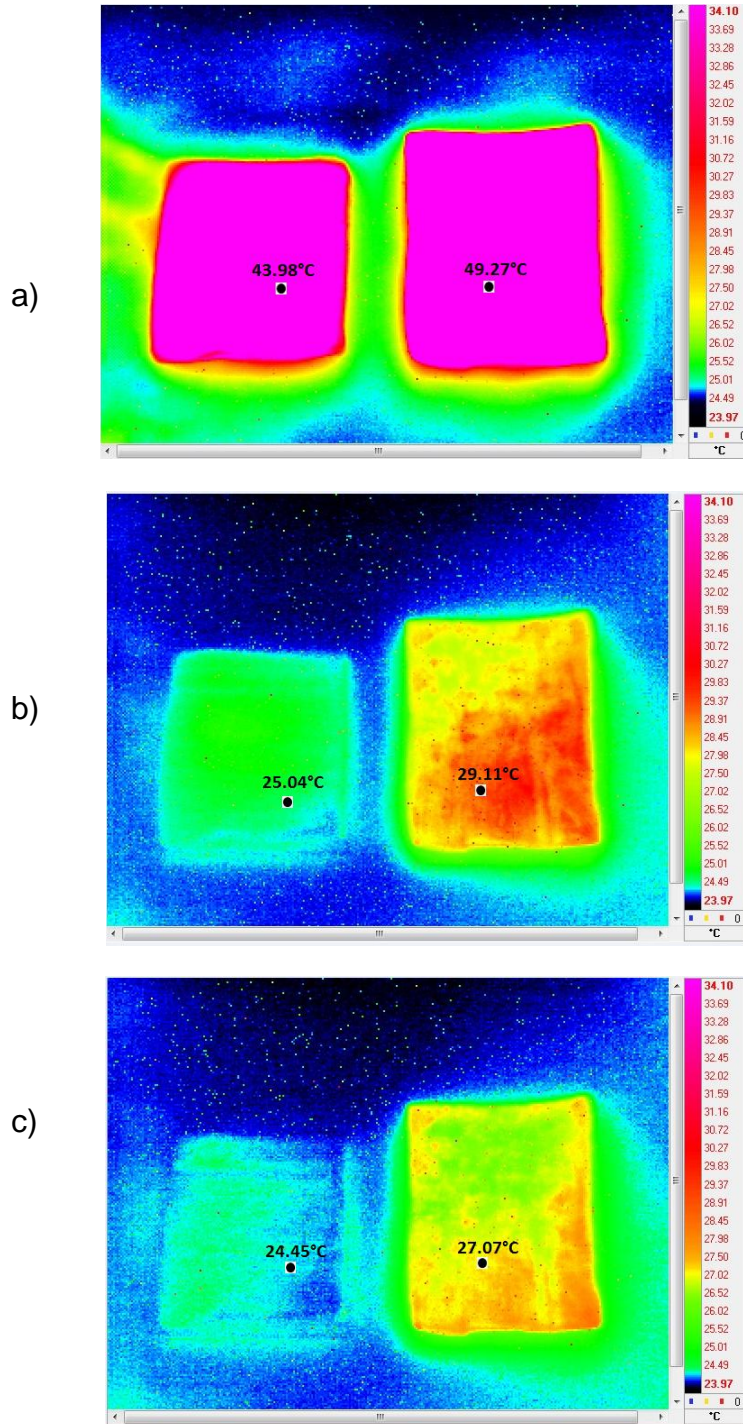


**Figure 31.** IR images of non-woven PLA unmodified (sample on the left) and modified with COPLA20 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

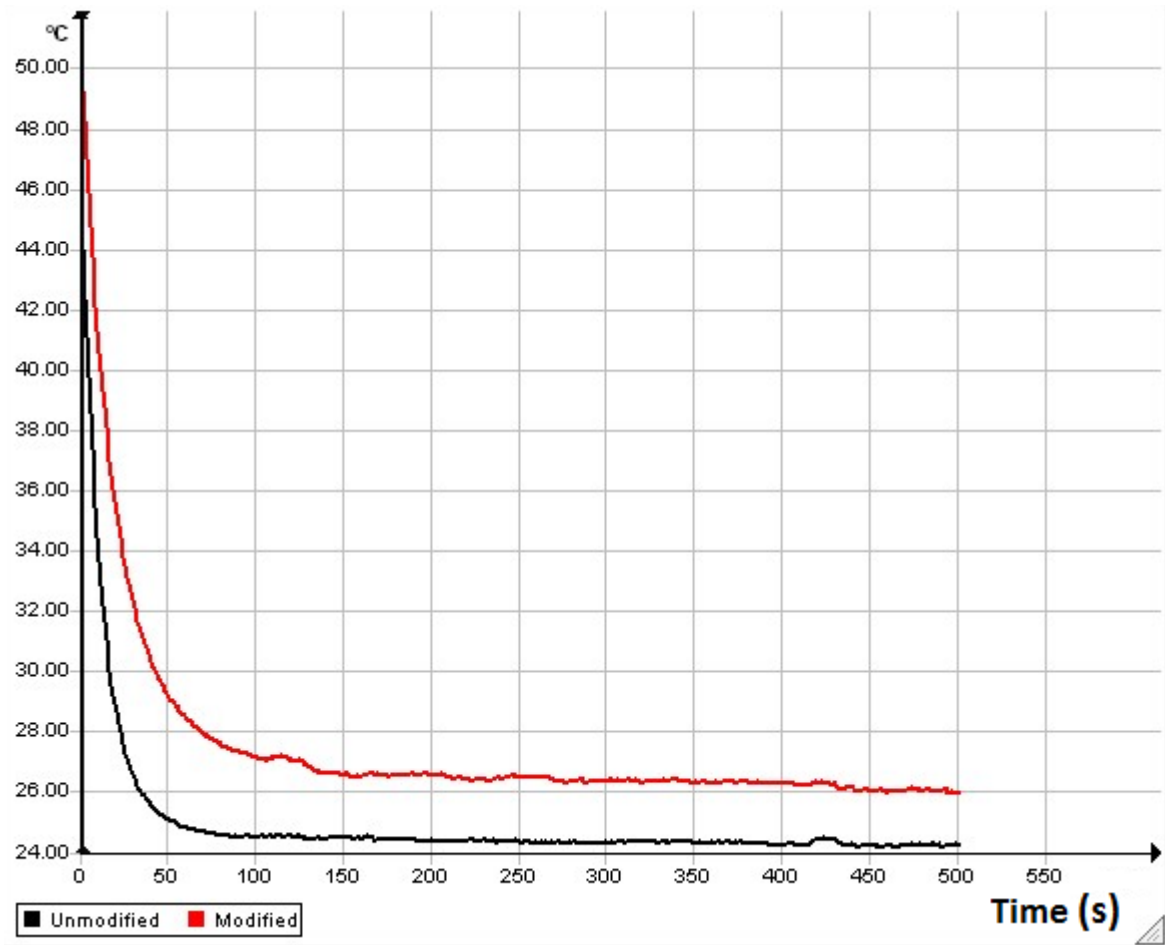


**Figure 32.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COPLA20 microcapsules and sodium alginate as binder.

## COPLA21 WITH SODIUM ALGinate.



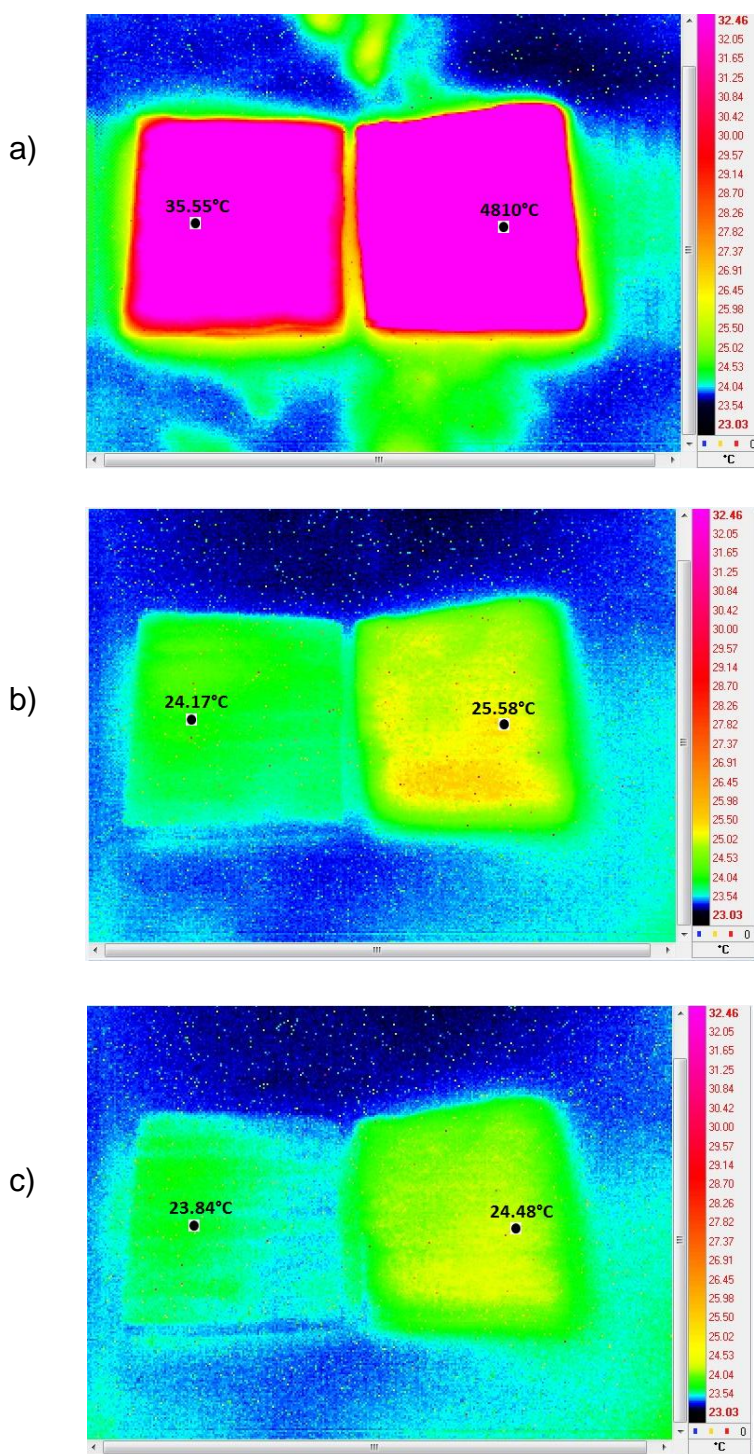
**Figure 33.** IR images of non-woven PLA unmodified (sample on the left) and modified with COPLA21 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.



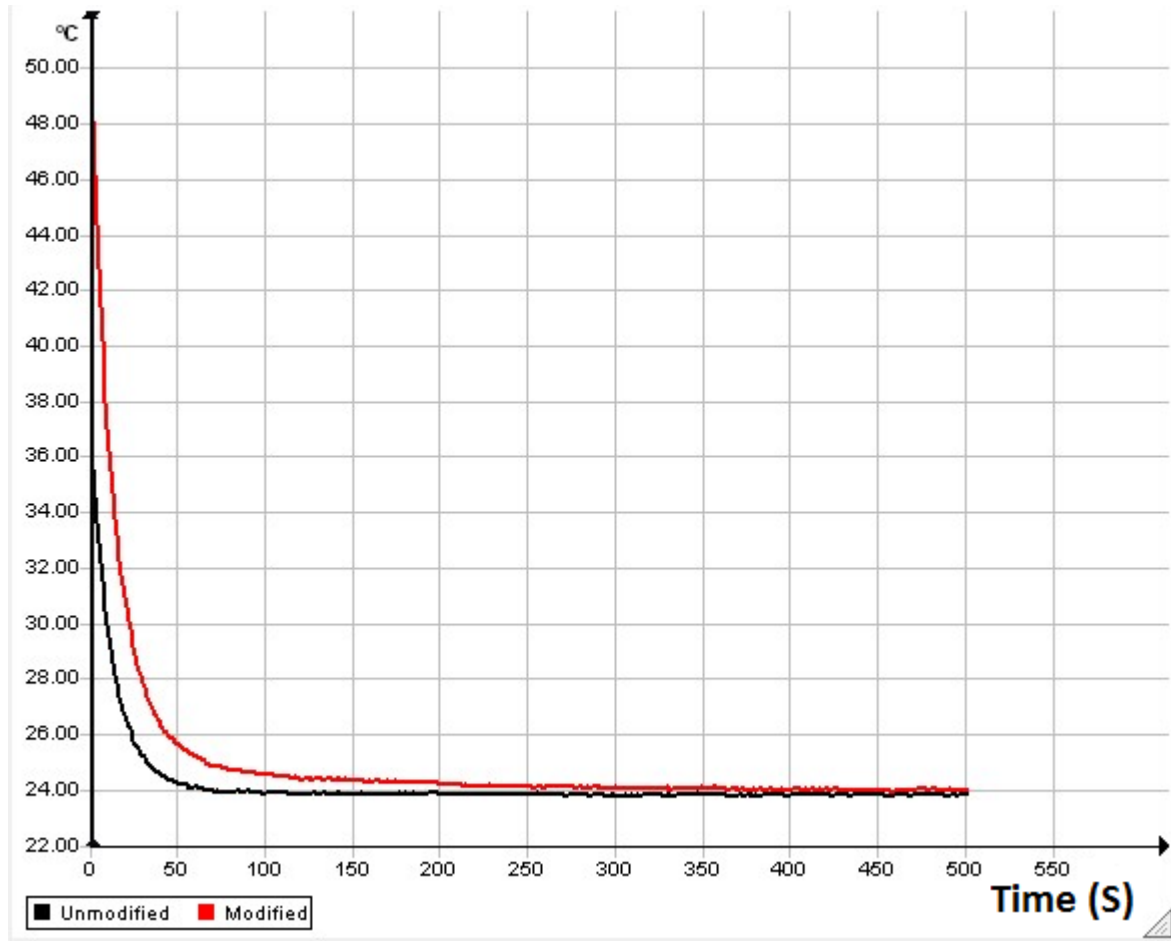
**Figure 34.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COPLA21 microcapsules and sodium alginate as binder.



## COEC3 WITH CHITOSAN.

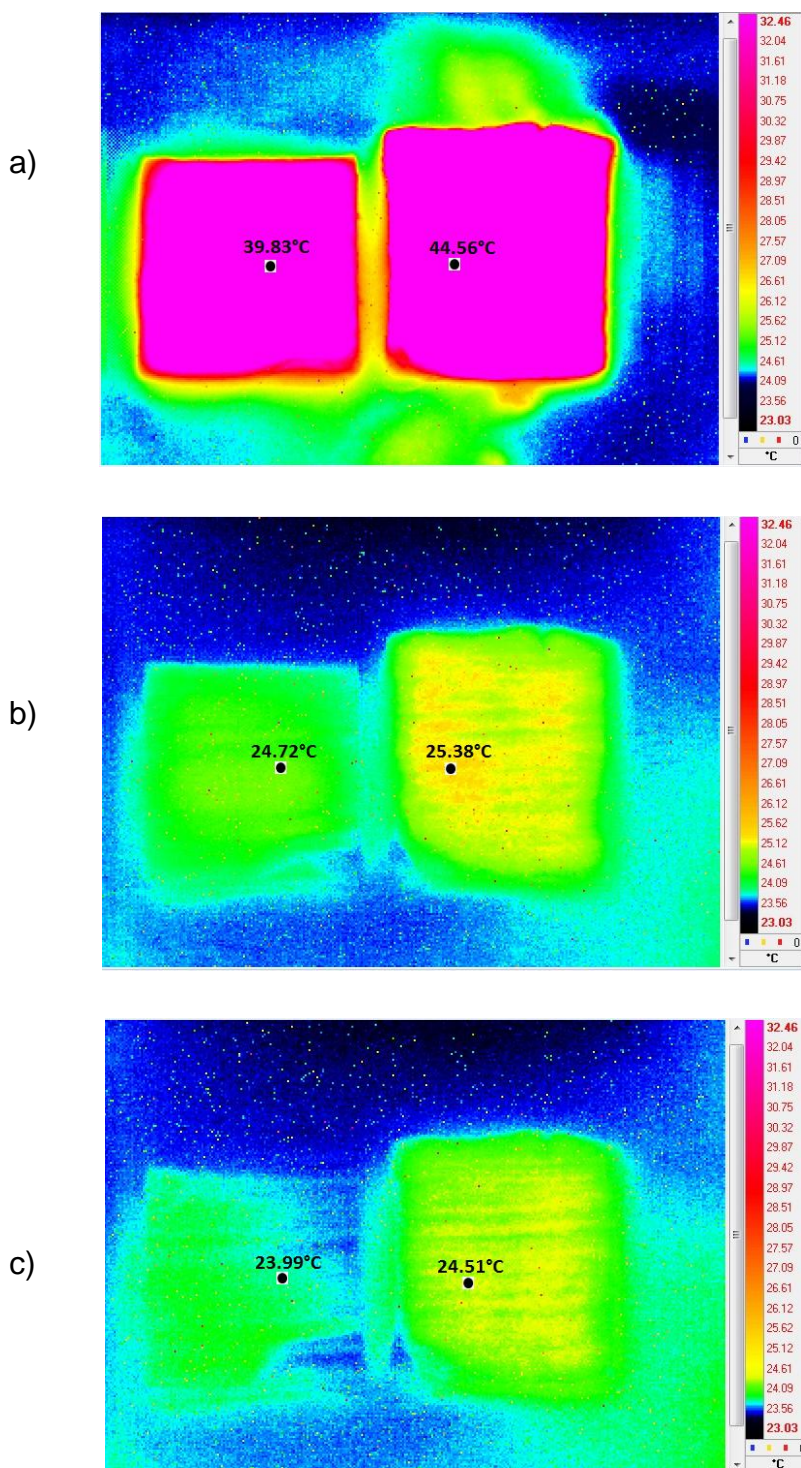


**Figure 35.** IR images of non-woven PLA unmodified (sample on the left) and modified with COEC3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating

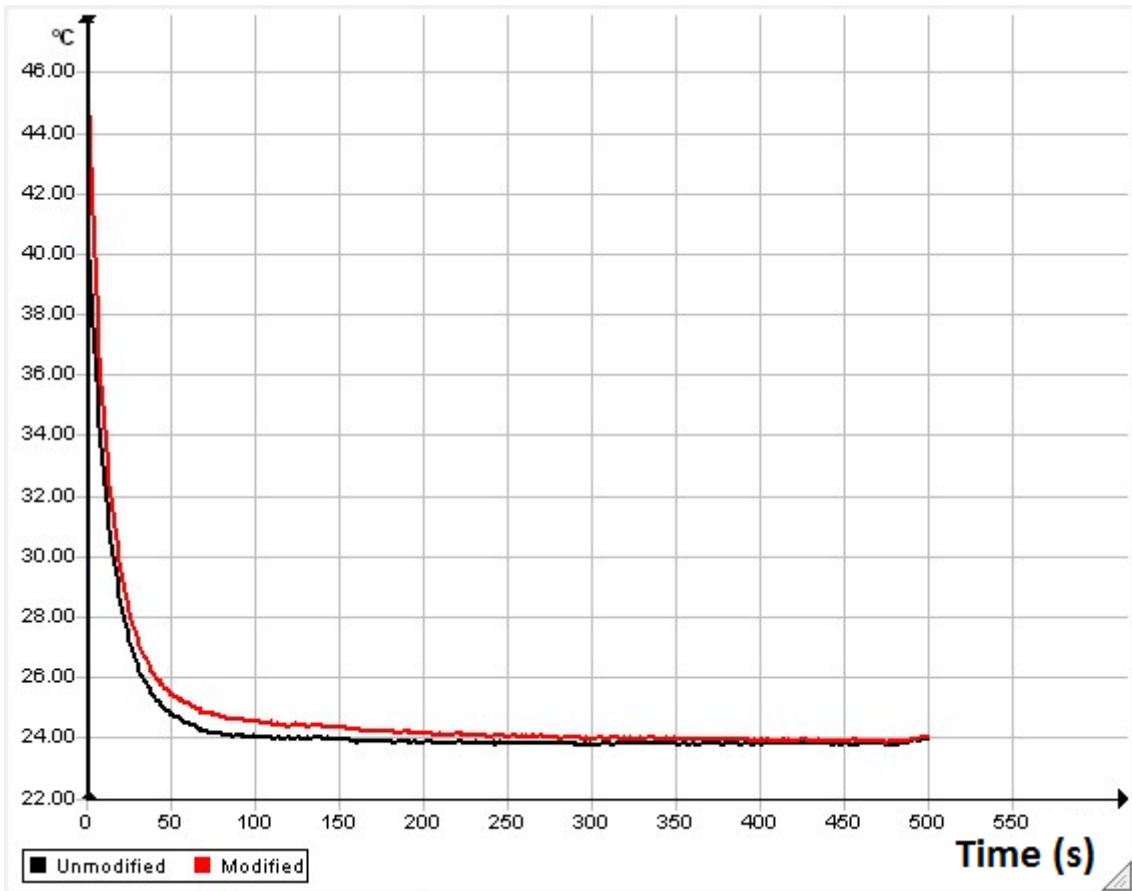


**Figure 36.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COEC3 microcapsules and chitosan as binder.

## COEC4 WITH CHITOSAN.

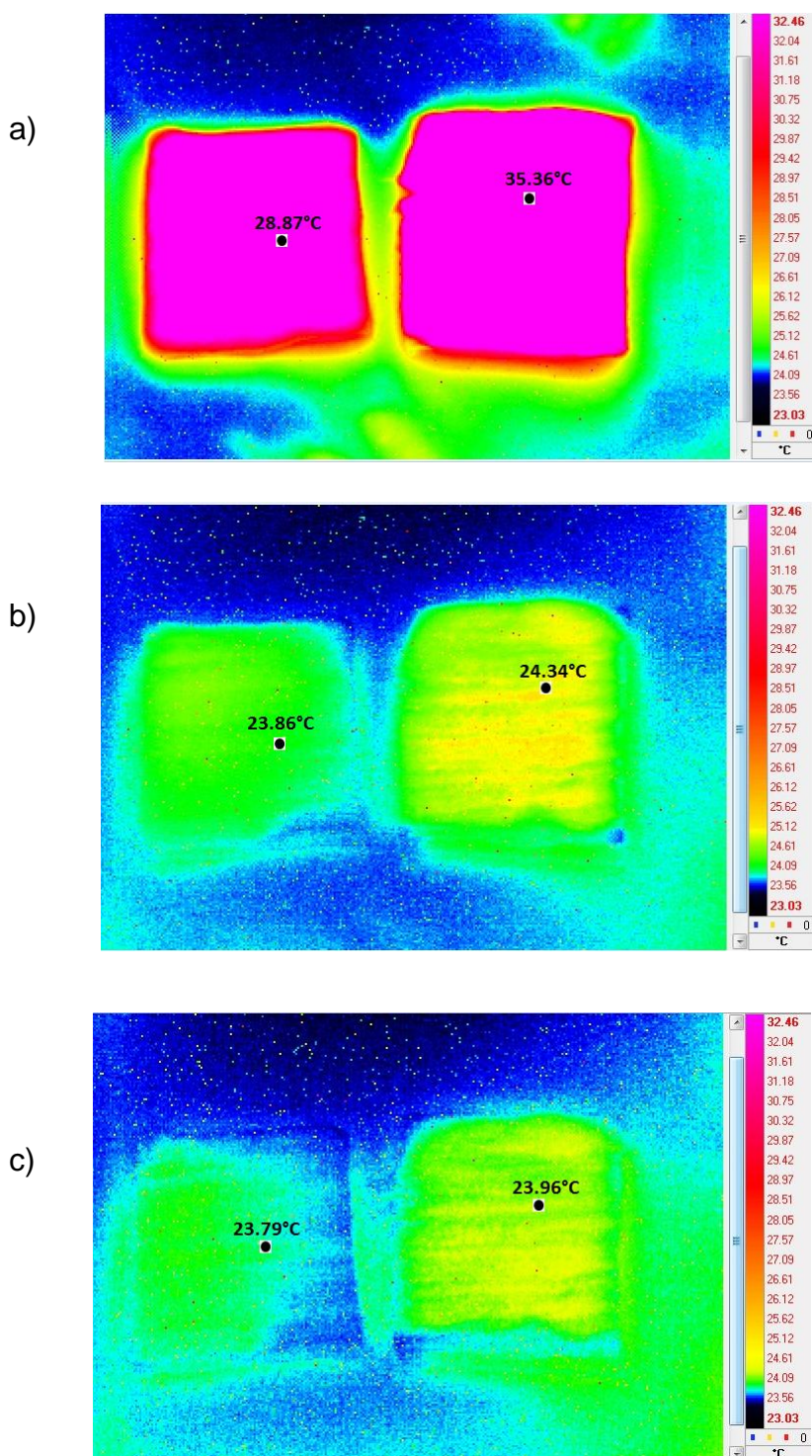


**Figure 37.** IR images of non-woven PLA unmodified (sample on the left) and modified with COEC4 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

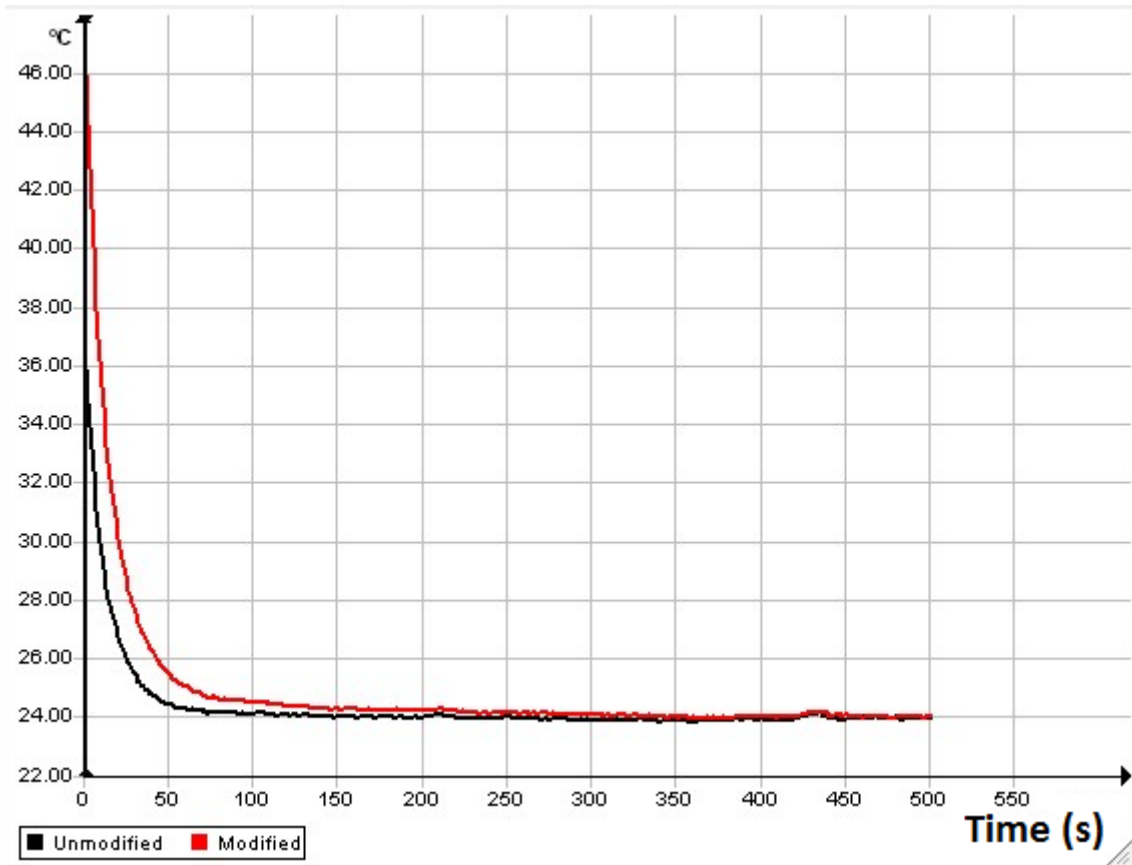


**Figure 38.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COEC4 microcapsules and chitosan as binder.

## COPLA20 WITH CHITOSAN.

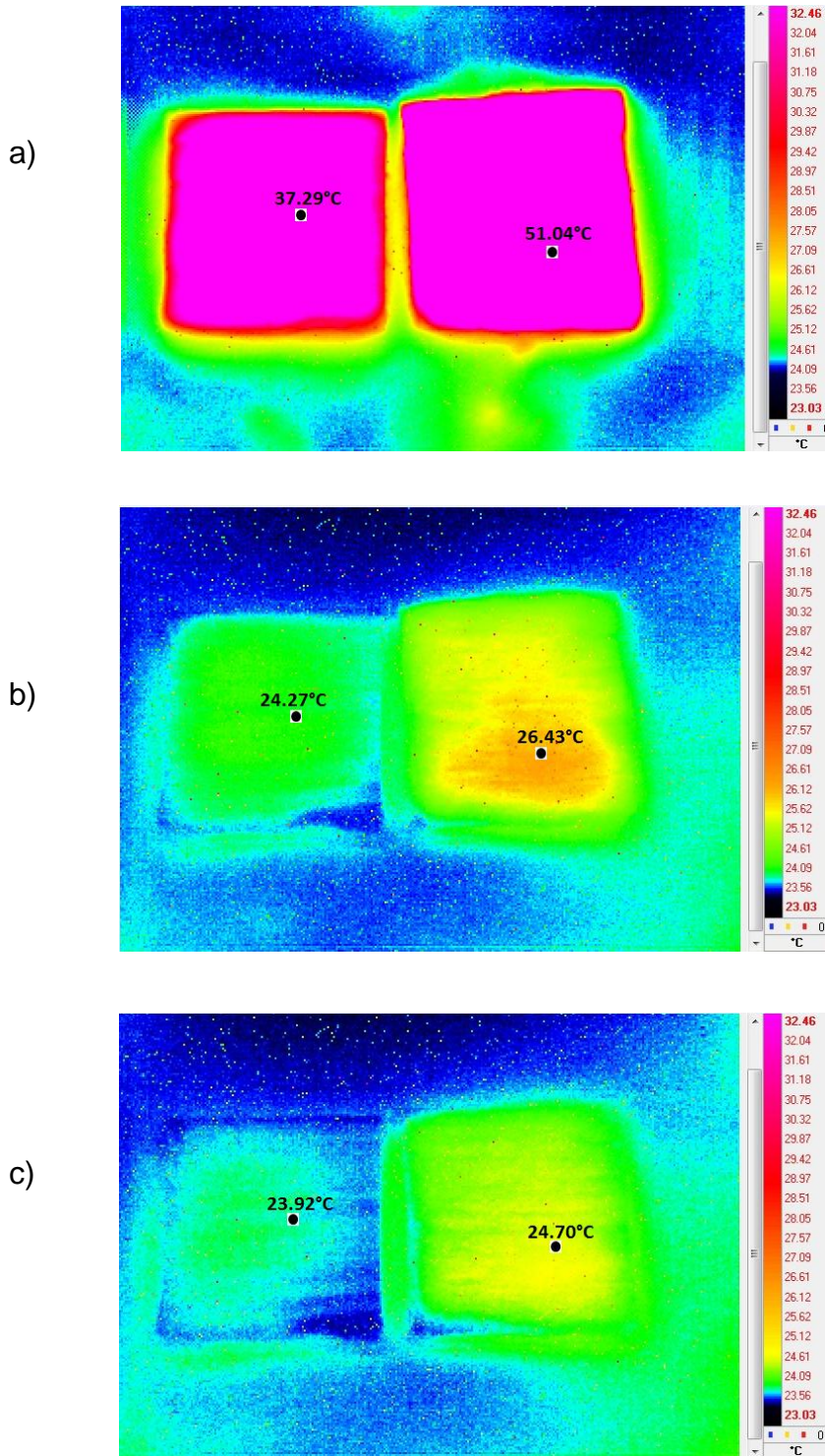


**Figure 39.** IR images of non-woven PLA unmodified (sample on the left) and modified with COPLA20 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

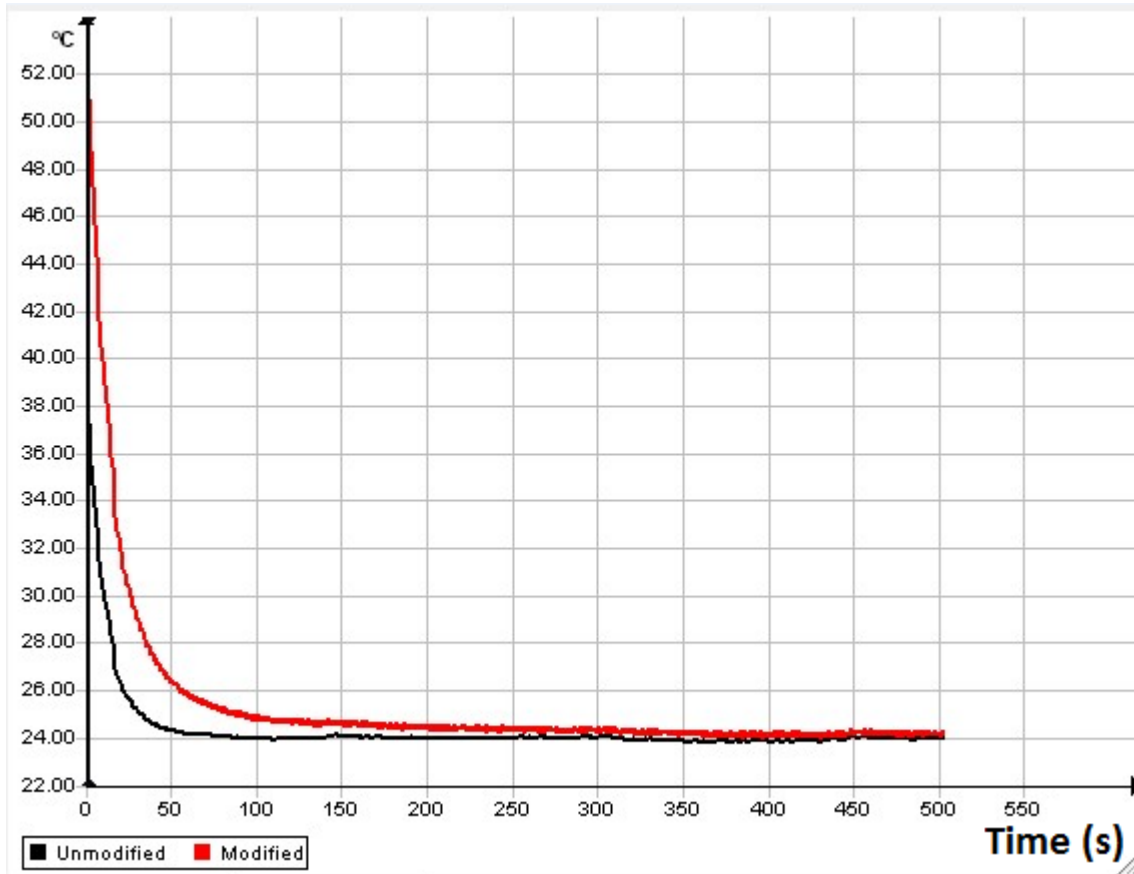


**Figure 40.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COPLA20 microcapsules and chitosan as binder.

**COPLA21 WITH CHITOSAN.**



**Figure 41.** IR images of non-woven PLA unmodified (sample on the left) and modified with COPLA21 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

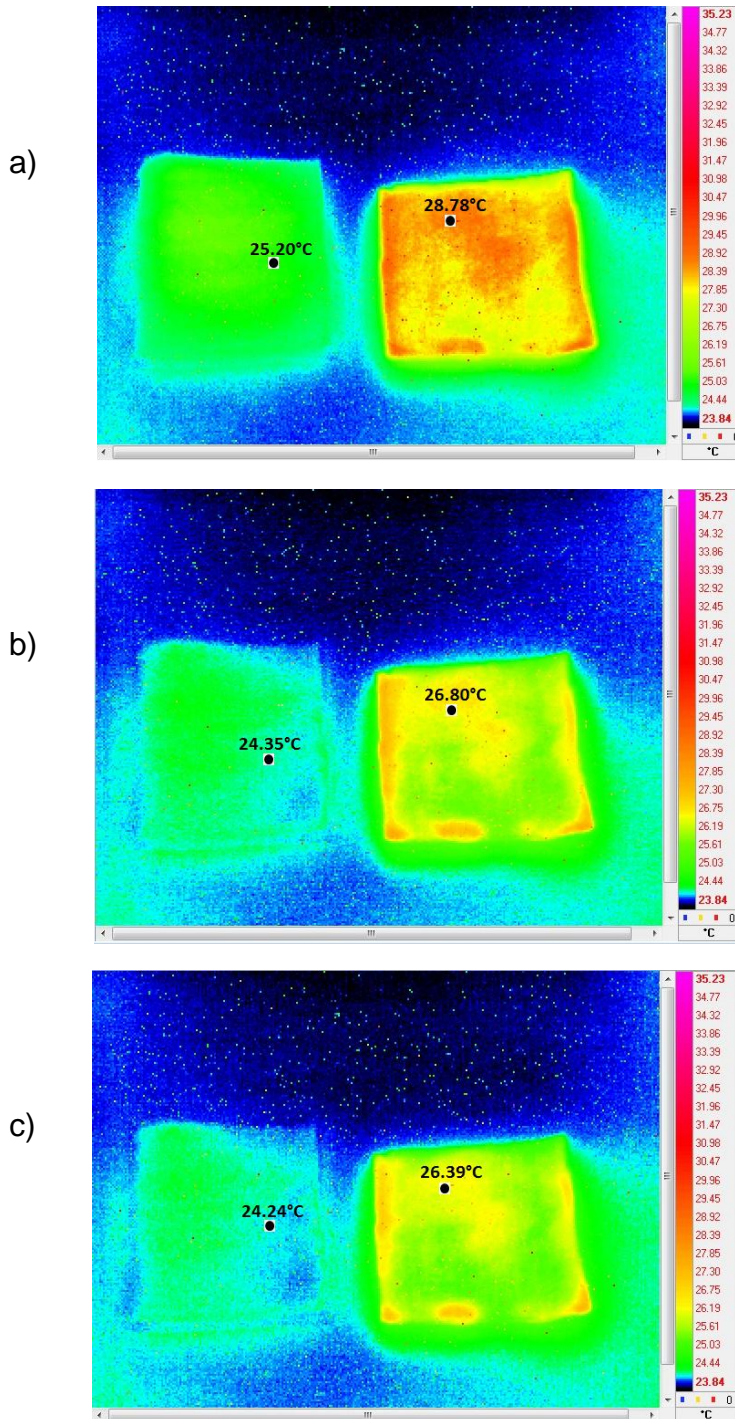


**Figure 42.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with COPLA21 microcapsules and chitosan as binder.

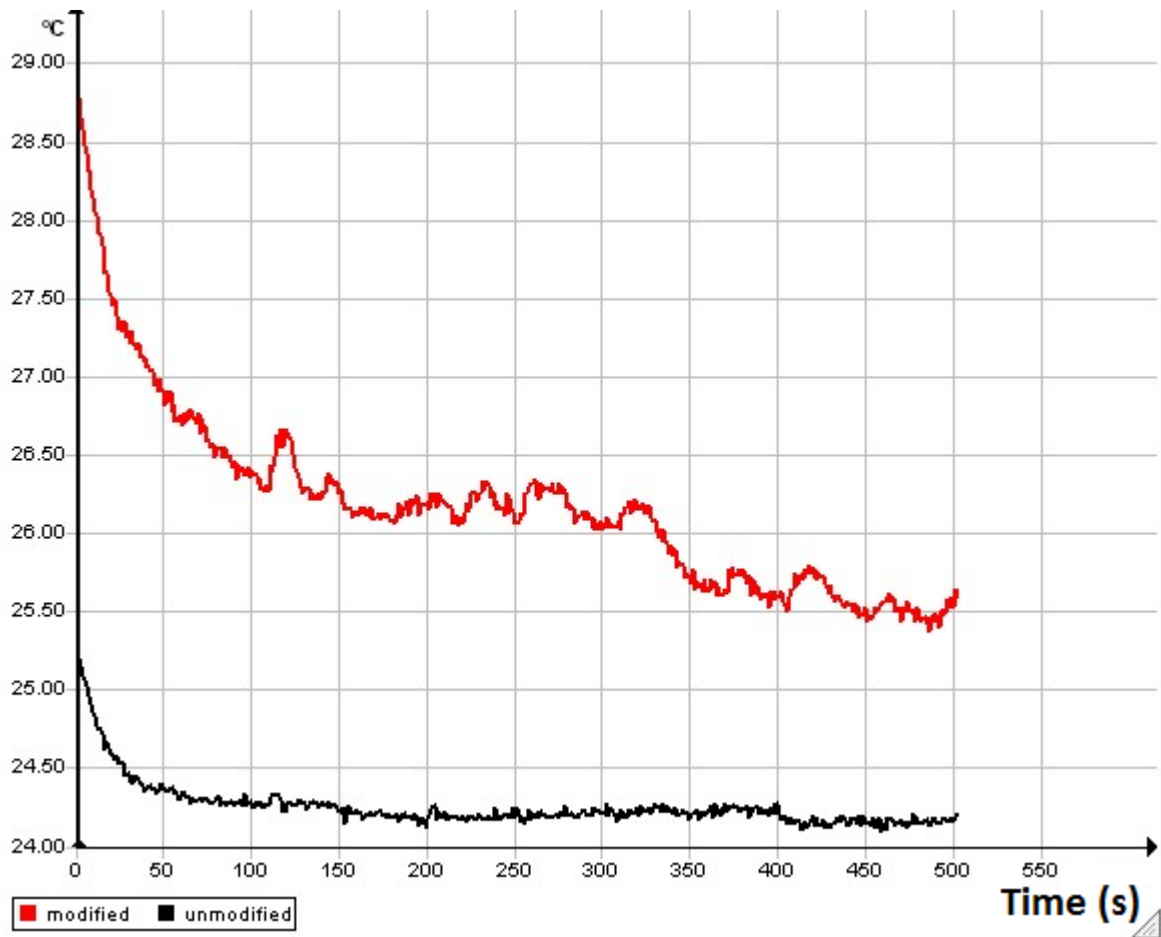


5.1.8.2. Modification of textiles with Bee wax microcapsules.

**BWEC2 WITH SODIUM ALGinate.**

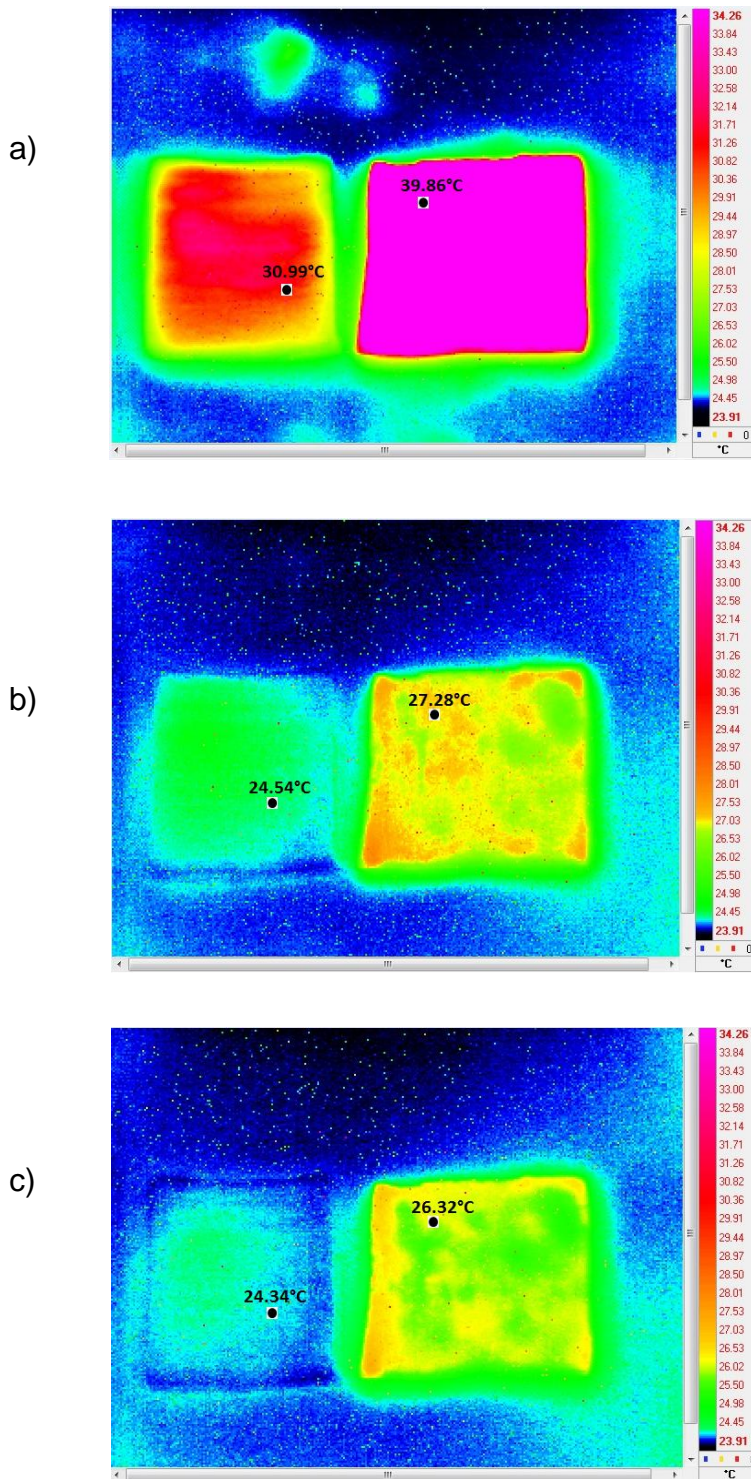


**Figure 43.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC2 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

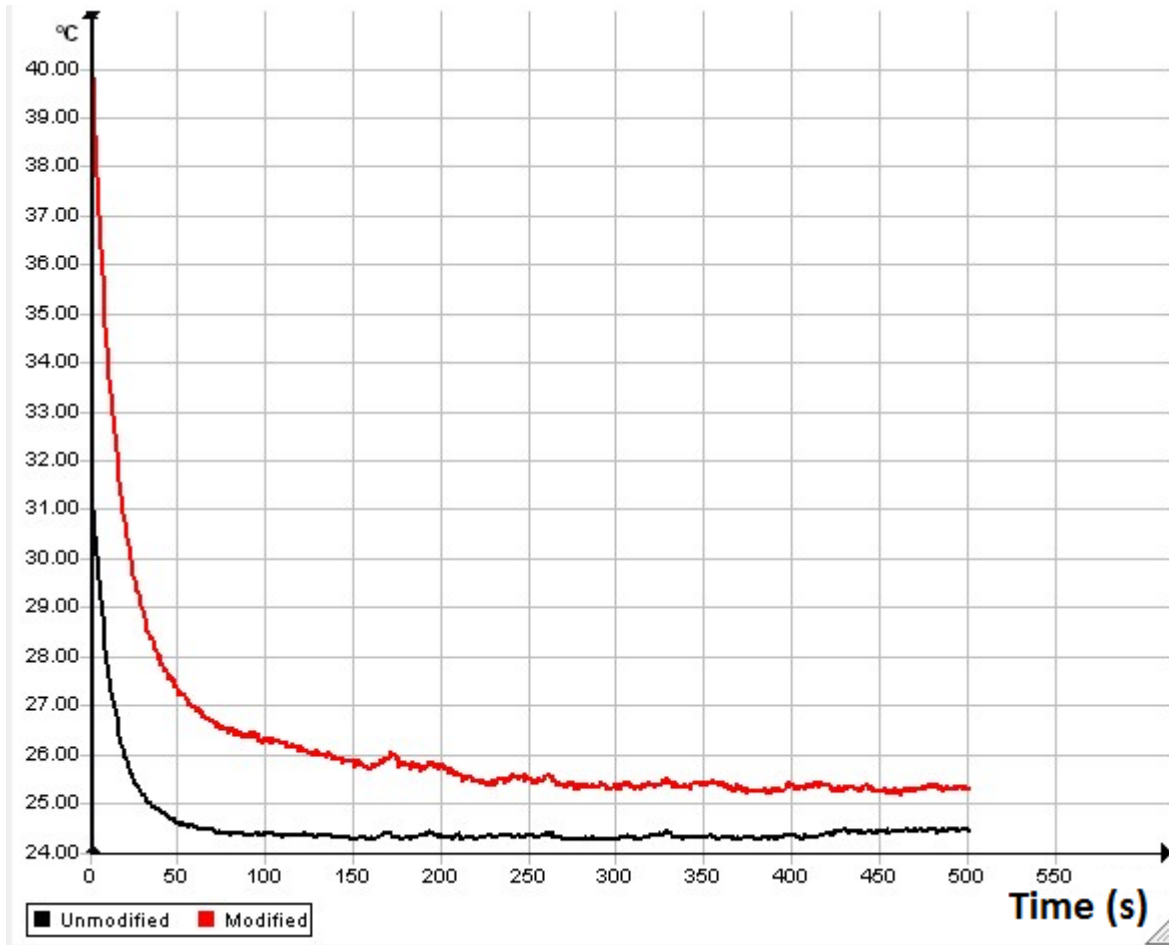


**Figure 44.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC2 microcapsules and sodium alginate as binder.

## BWPLA2 WITH SODIUM ALGINATE.

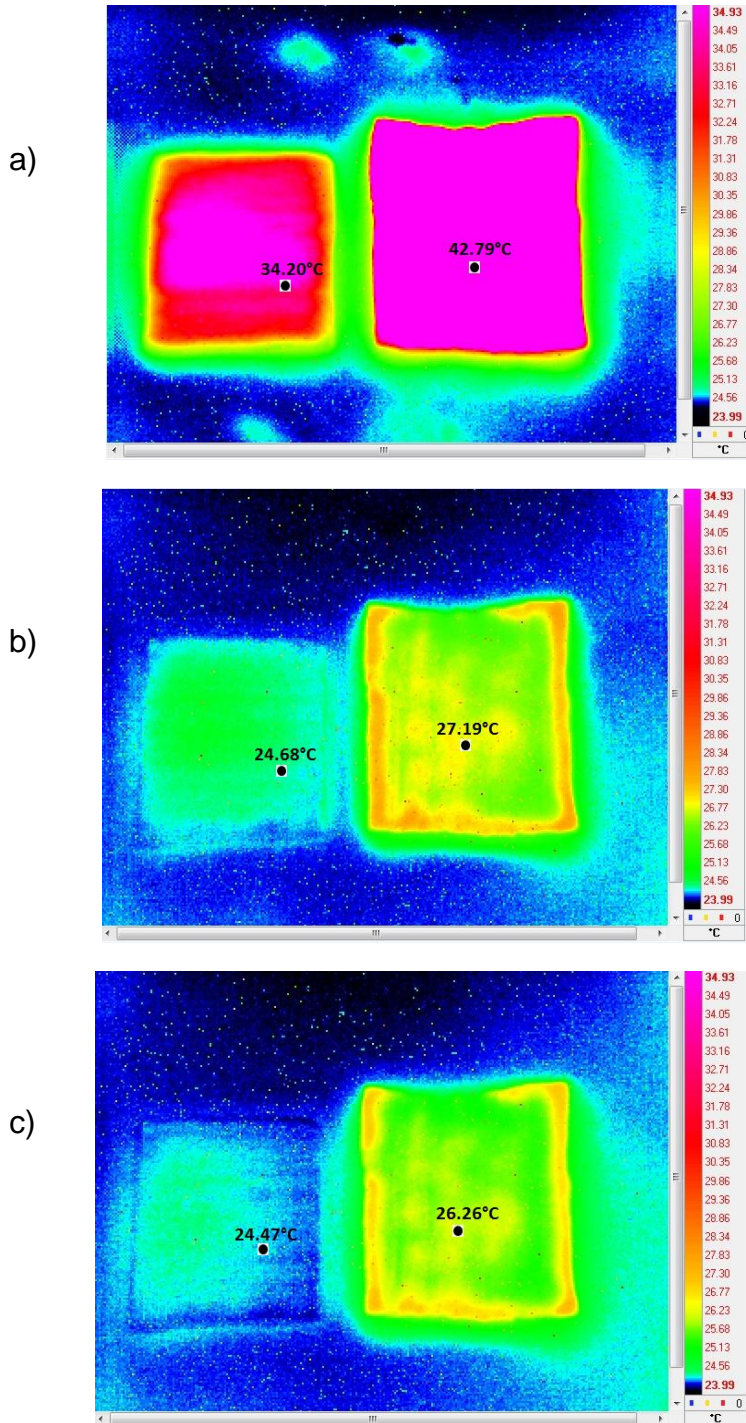


**Figure 45.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWPLA2 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

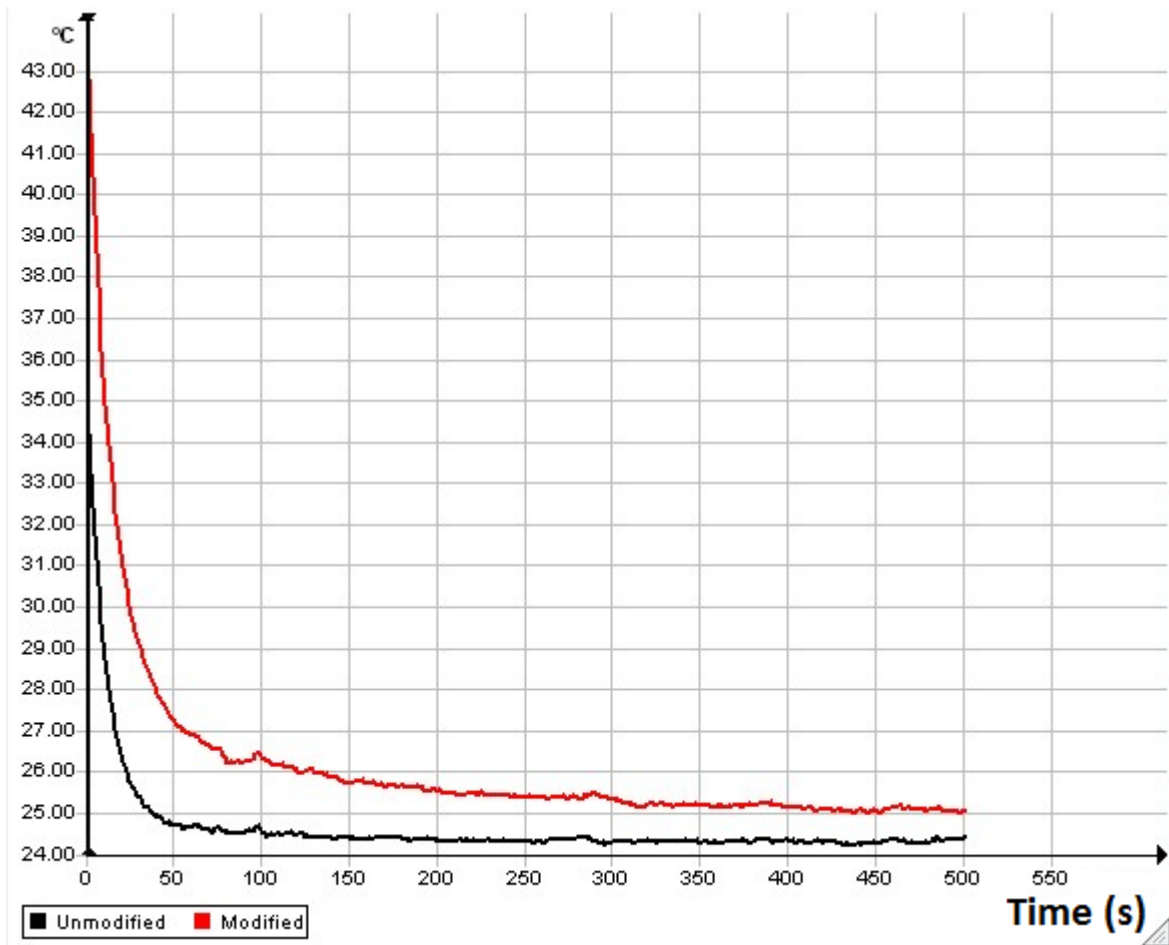


**Figure 46.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWPLA2 microcapsules and sodium alginate as binder.

**BWPLA3 WITH SODIUM ALGINATE.**

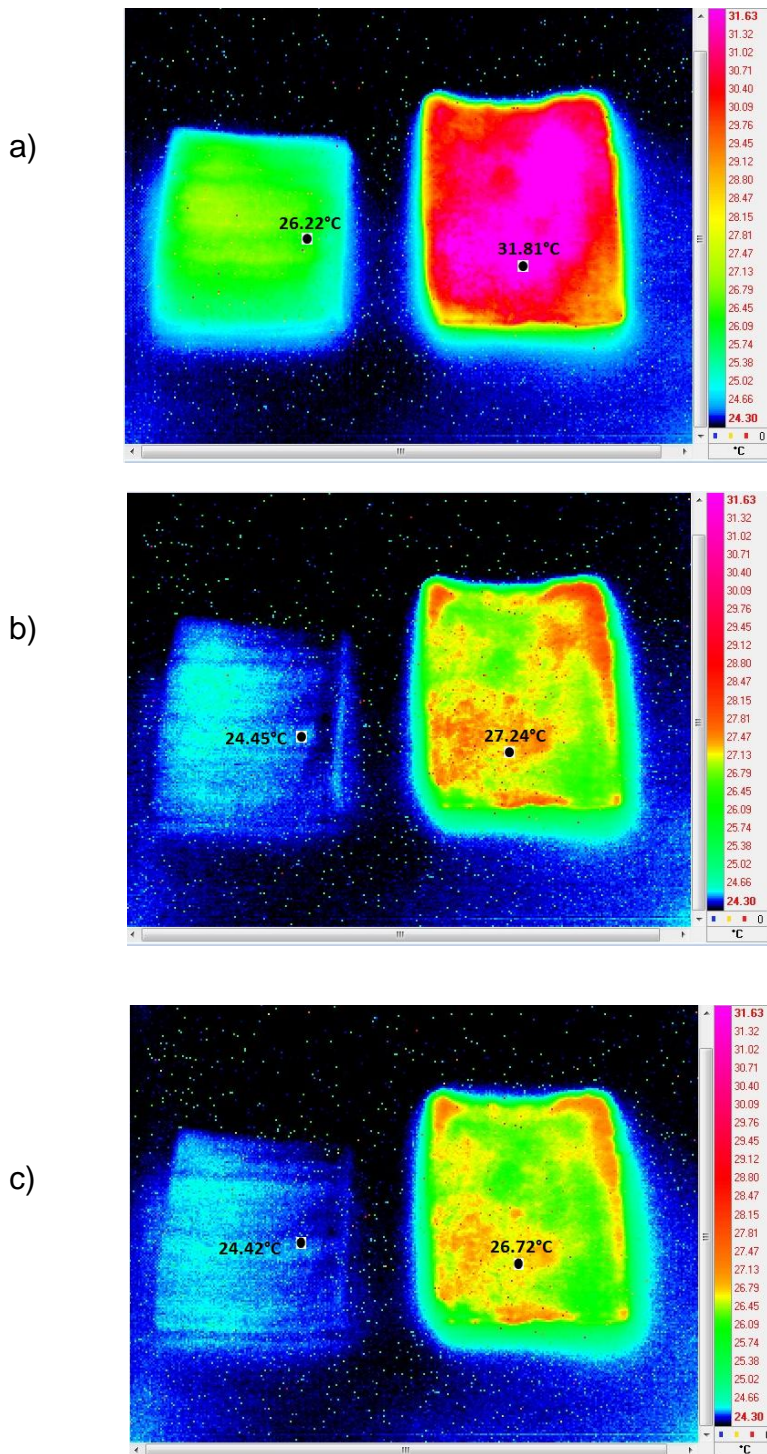


**Figure 47.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWPLA3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

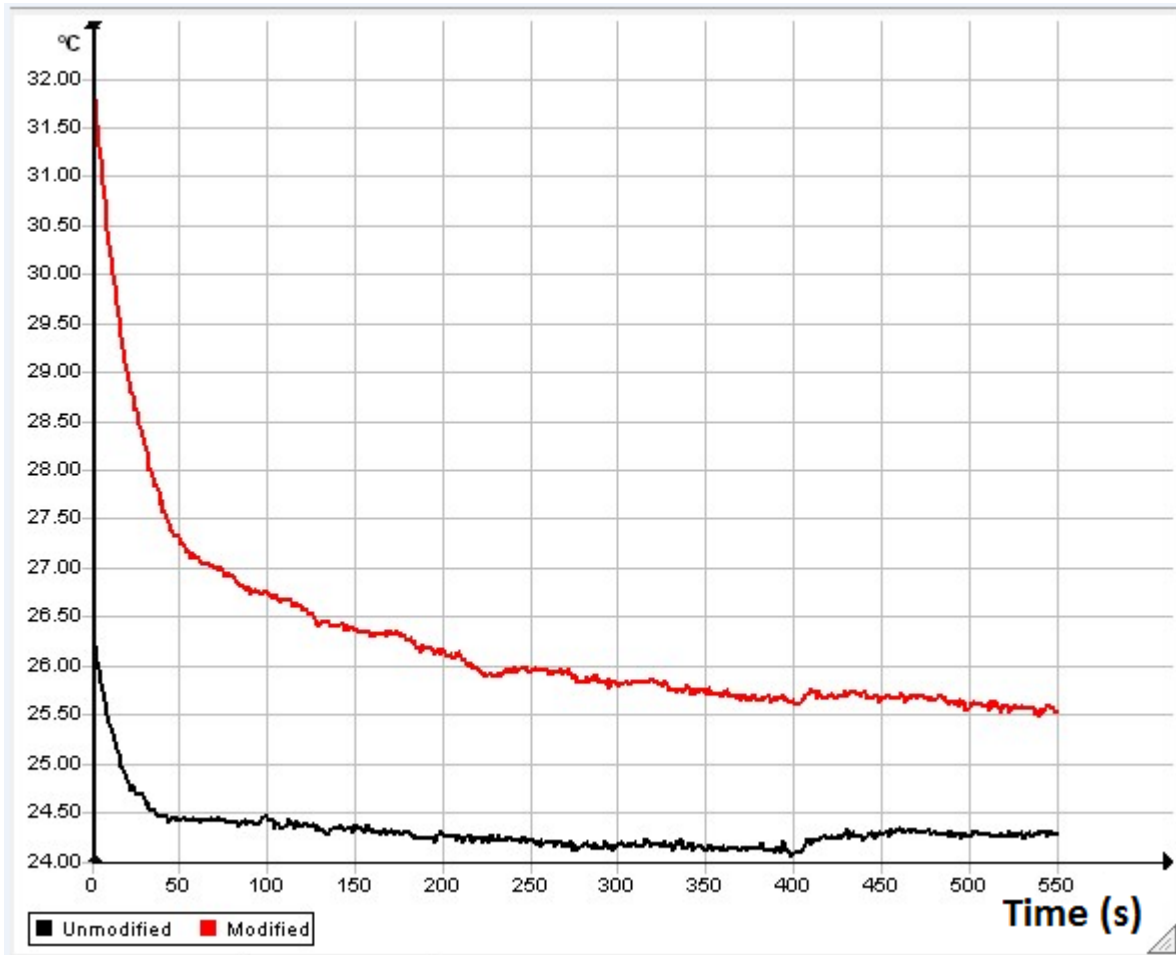


**Figure 48.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWPLA3 microcapsules and sodium alginate as binder.

## BWEC3 WITH SODIUM ALGinate



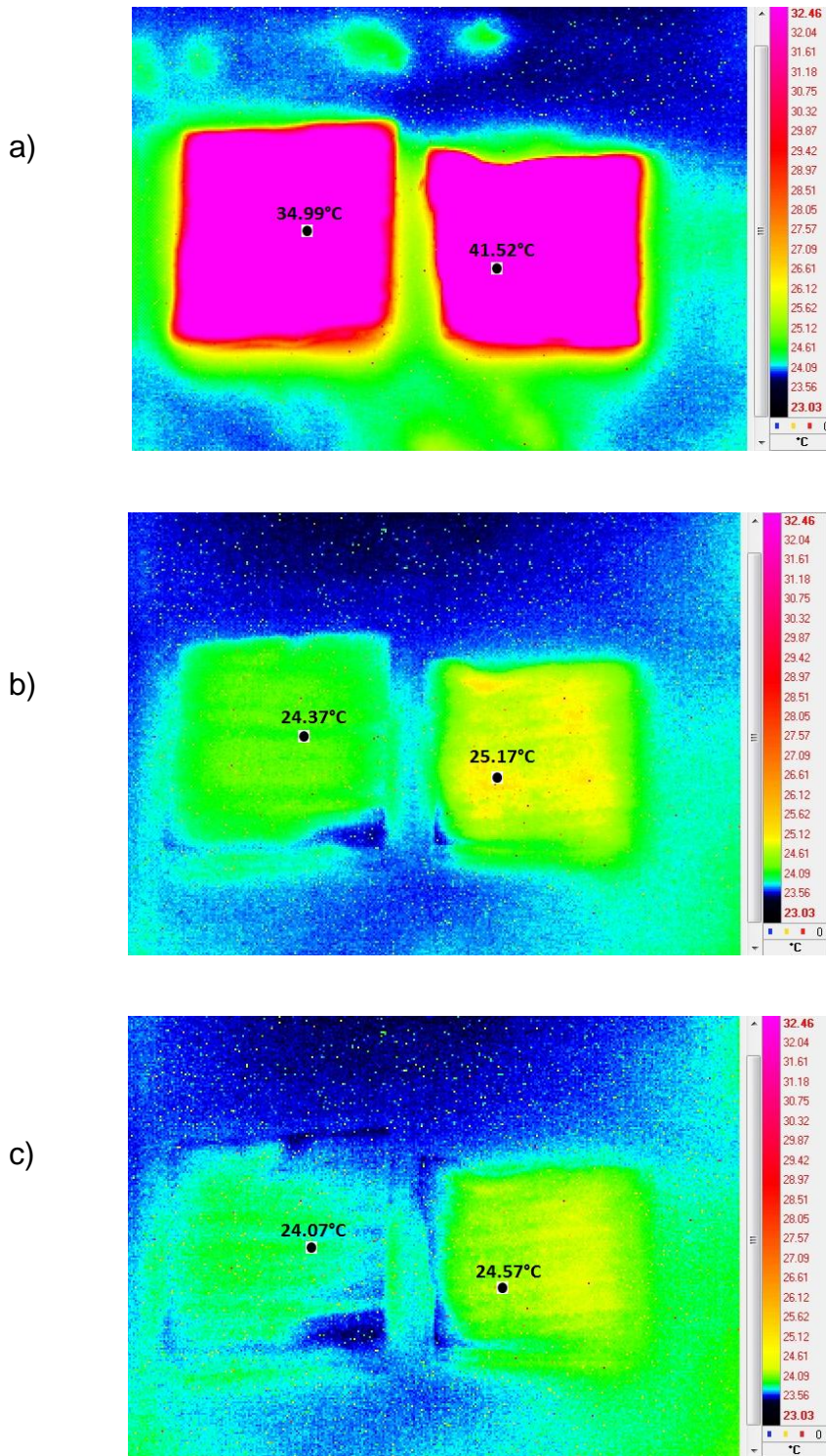
**Figure 49.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.



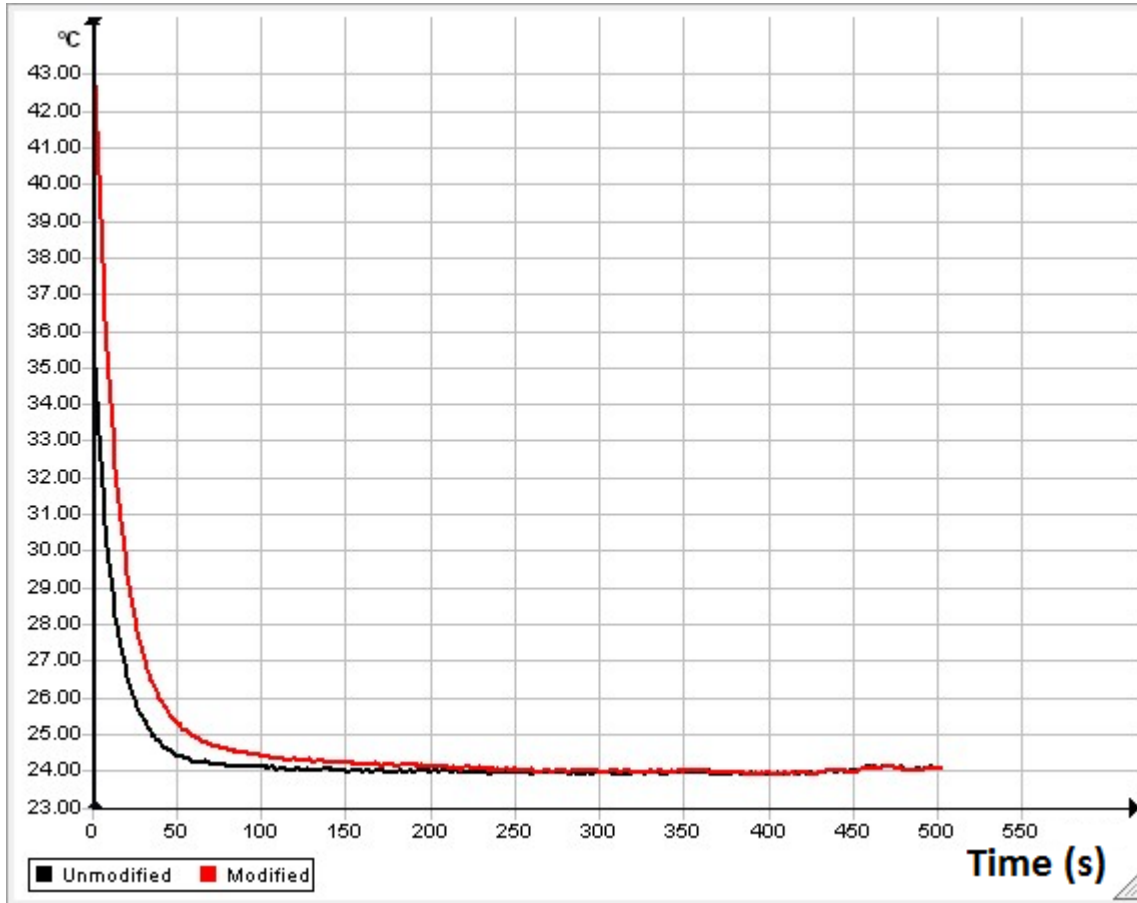
**Figure 50.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC3 microcapsules and sodium alginate as binder.



## BWEC2 WITH CHITOSAN.

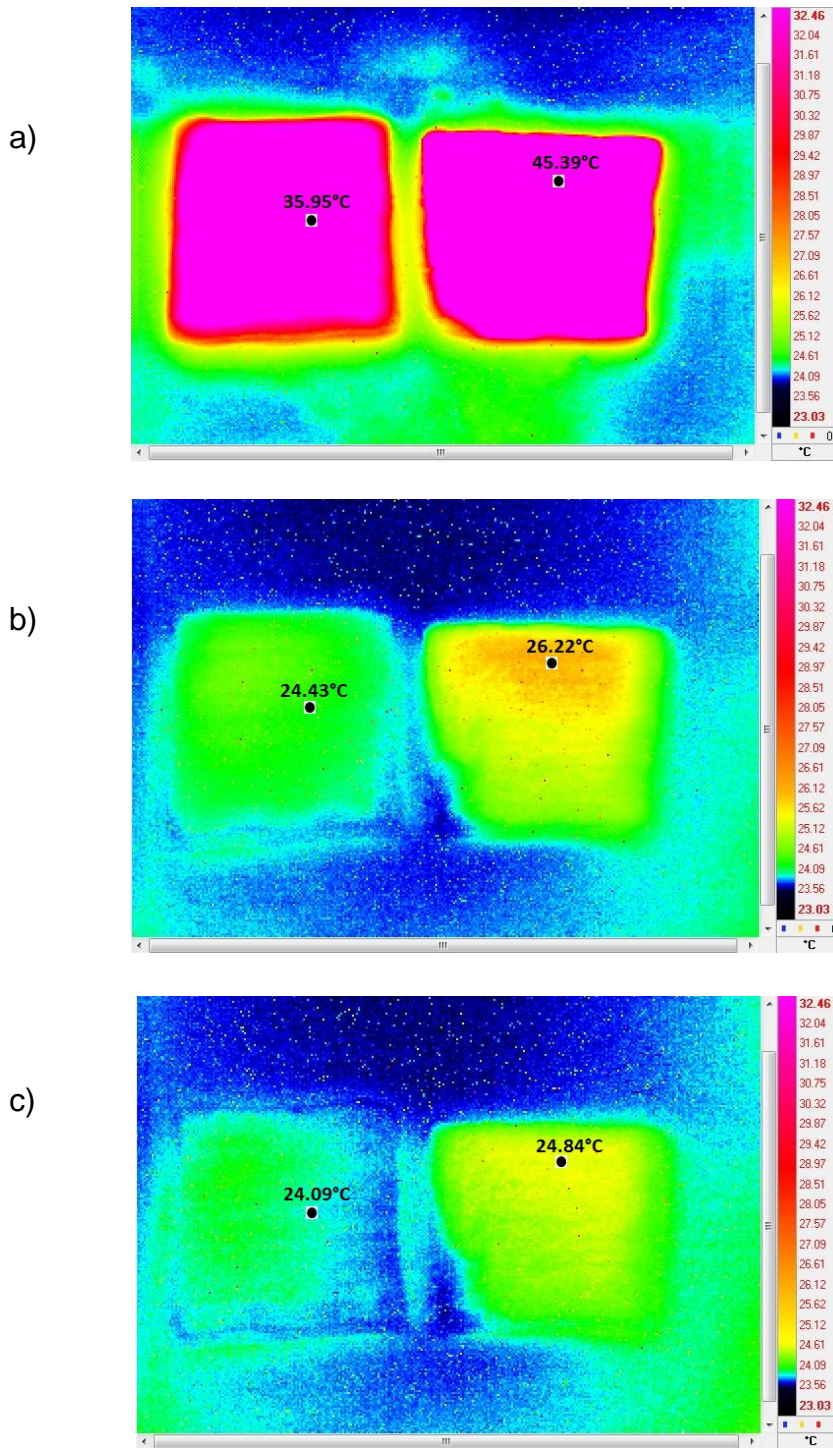


**Figure 51.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC2 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

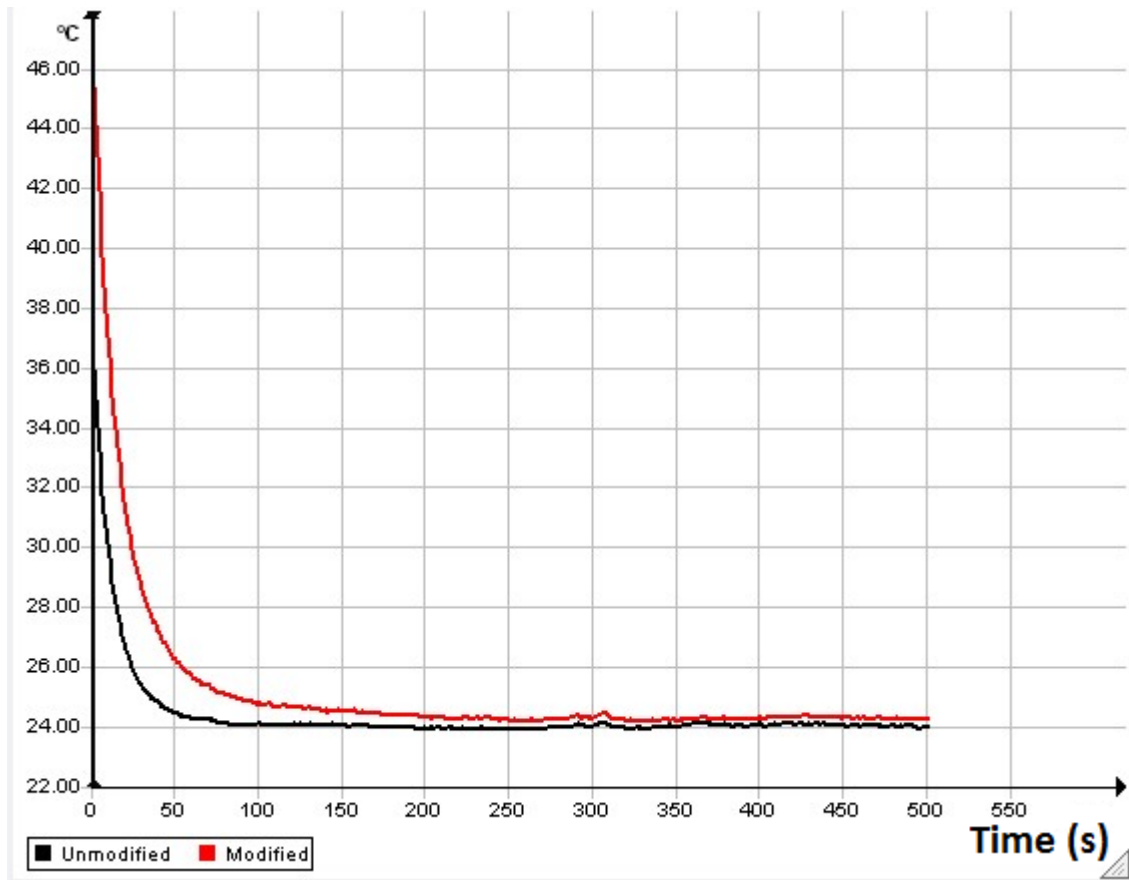


**Figure 52.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC2 microcapsules and chitosan as binder.

## BWPLA2 WITH CHITOSAN.

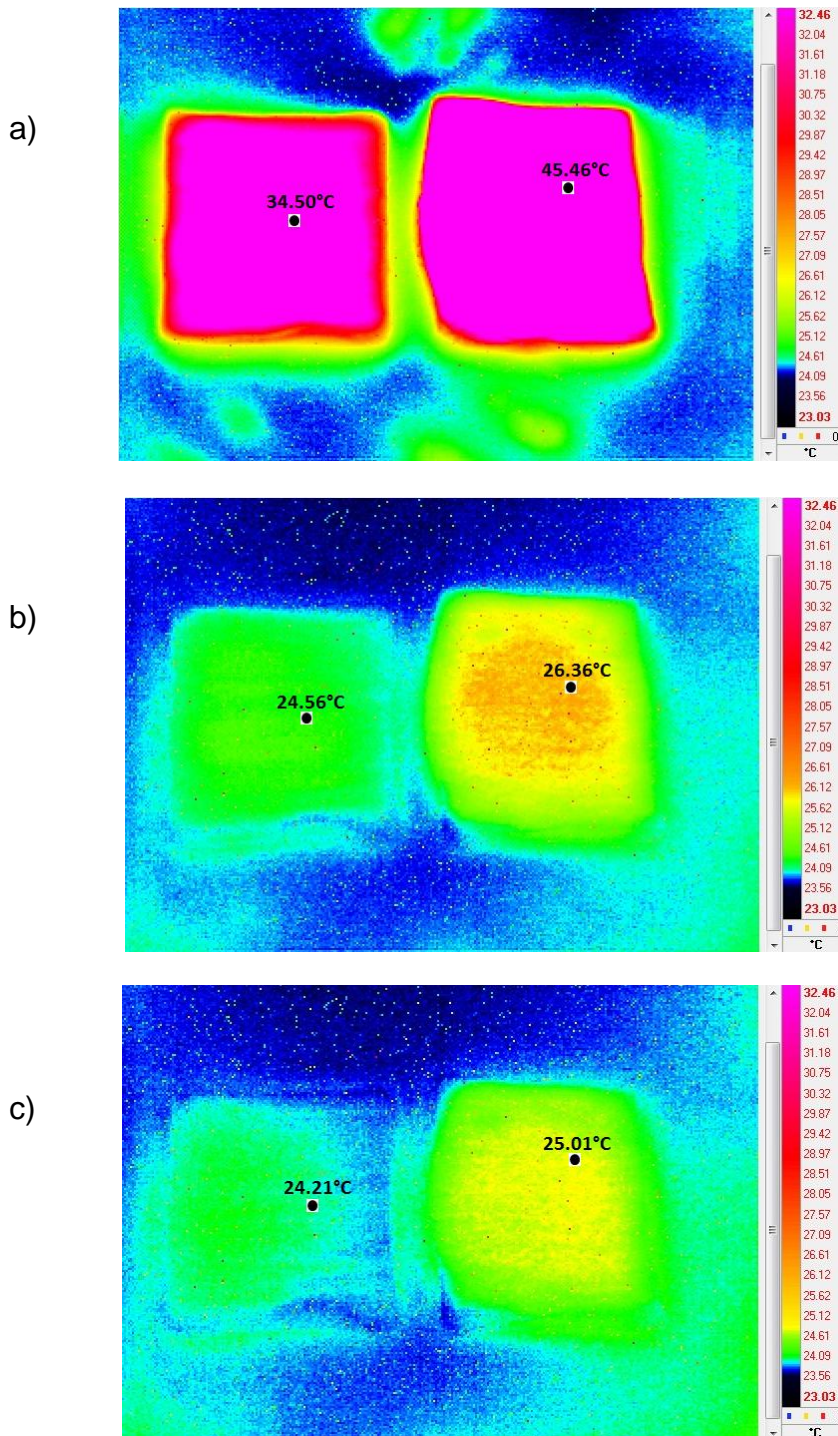


**Figure 53.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWPLA2 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

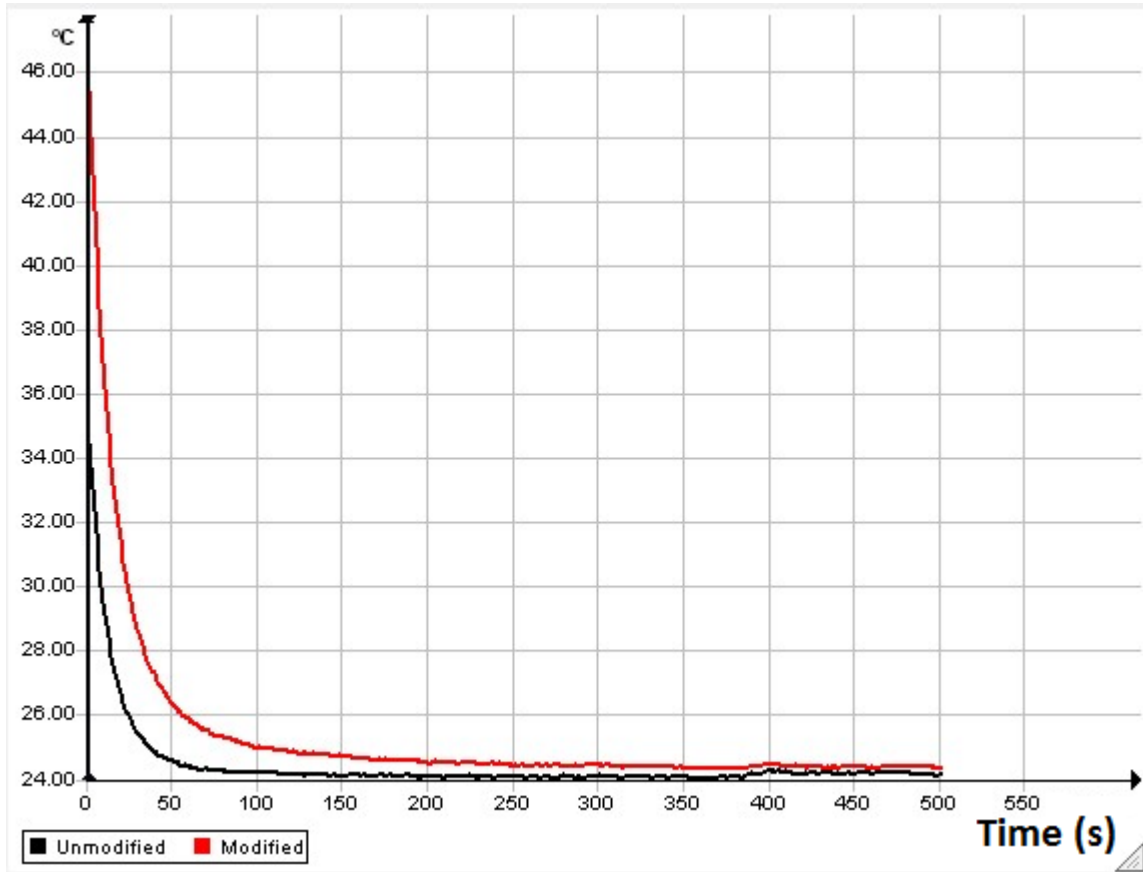


**Figure 54.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWPLA2 microcapsules and chitosan as binder.

## BWPLA3 WITH CHITOSAN.

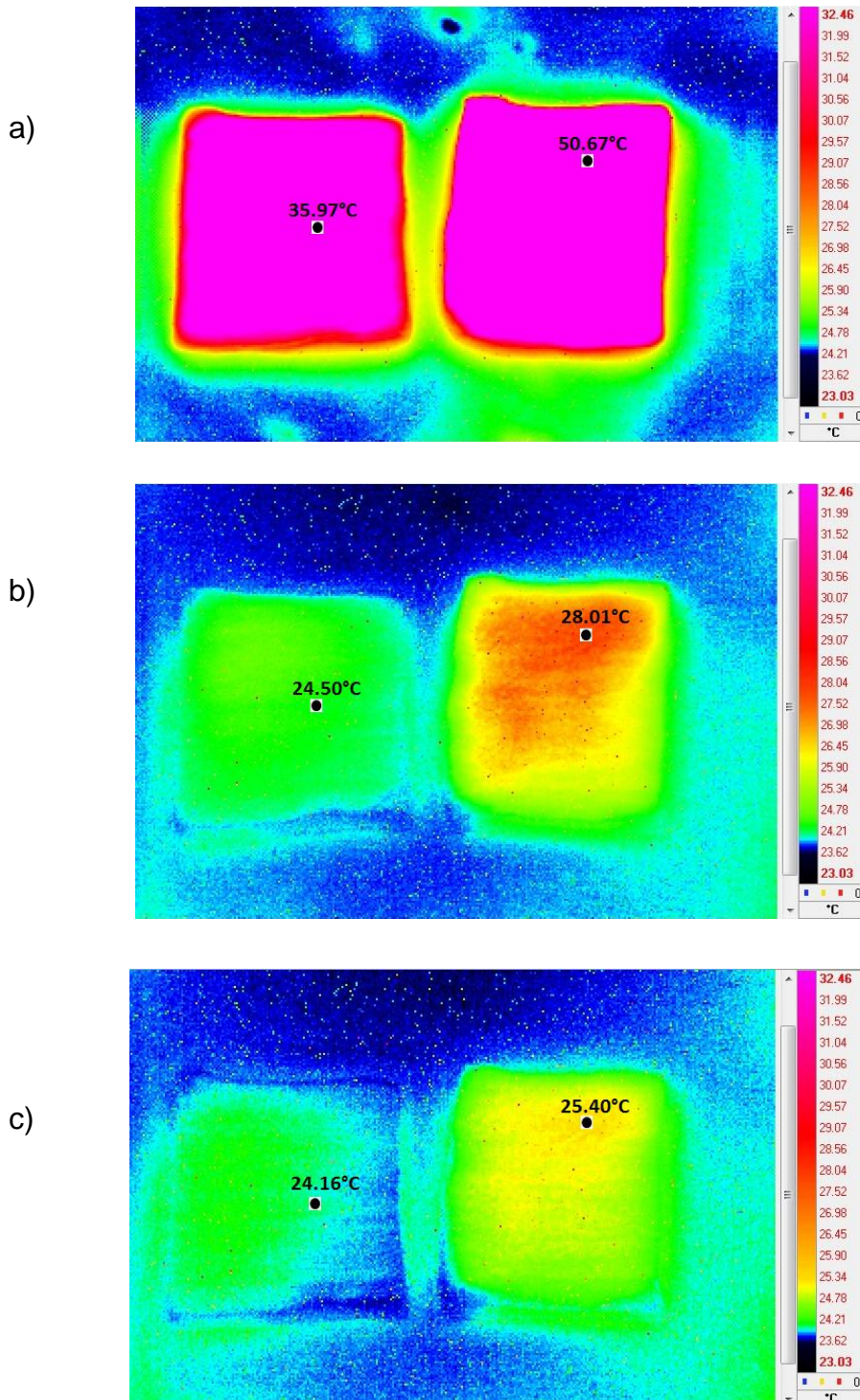


**Figure 55.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWPLA3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

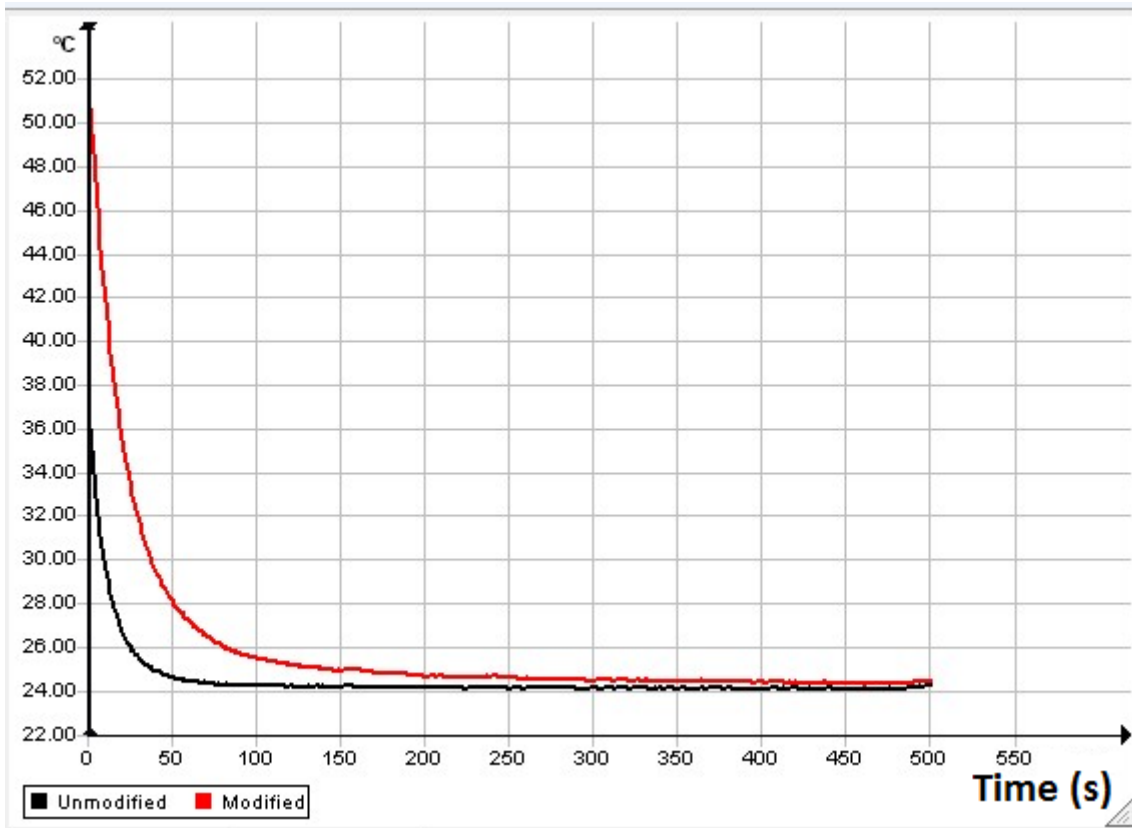


**Figure 56.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWPLA3 microcapsules and chitosan as binder.

## BWEC3 WITH CHITOSAN.



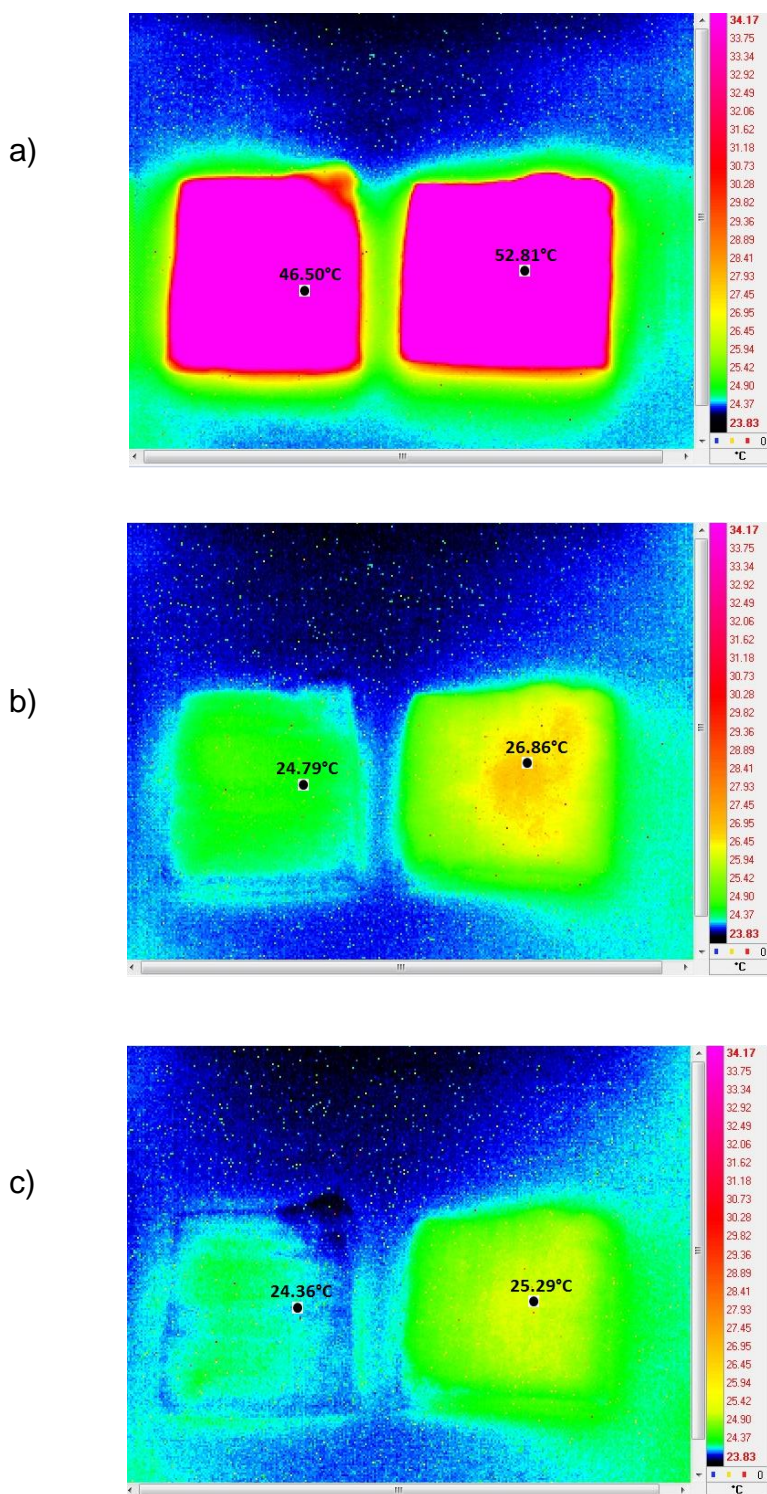
**Figure 57.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.



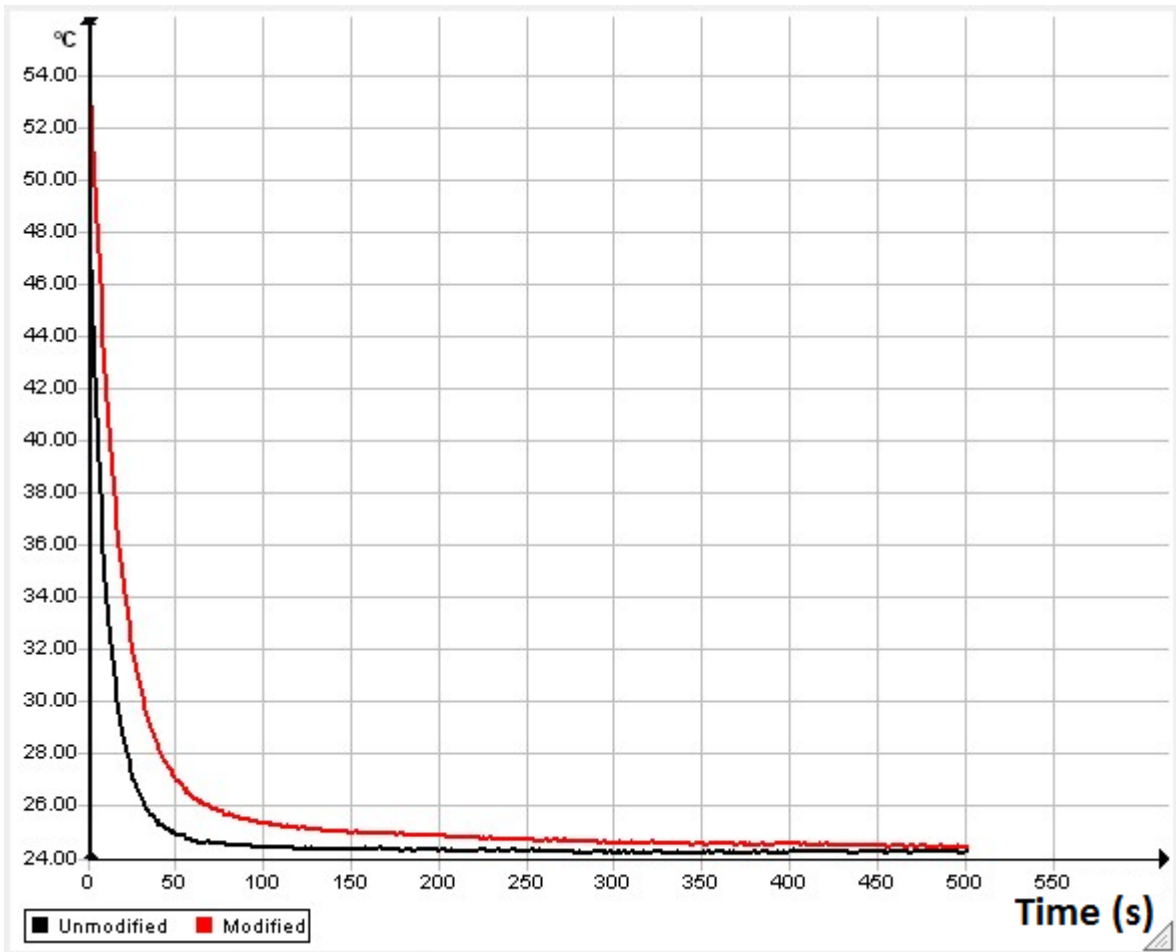
**Figure 58.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC3 microcapsules and chitosan as binder.



## BWEC4 WITH CHITOSAN.

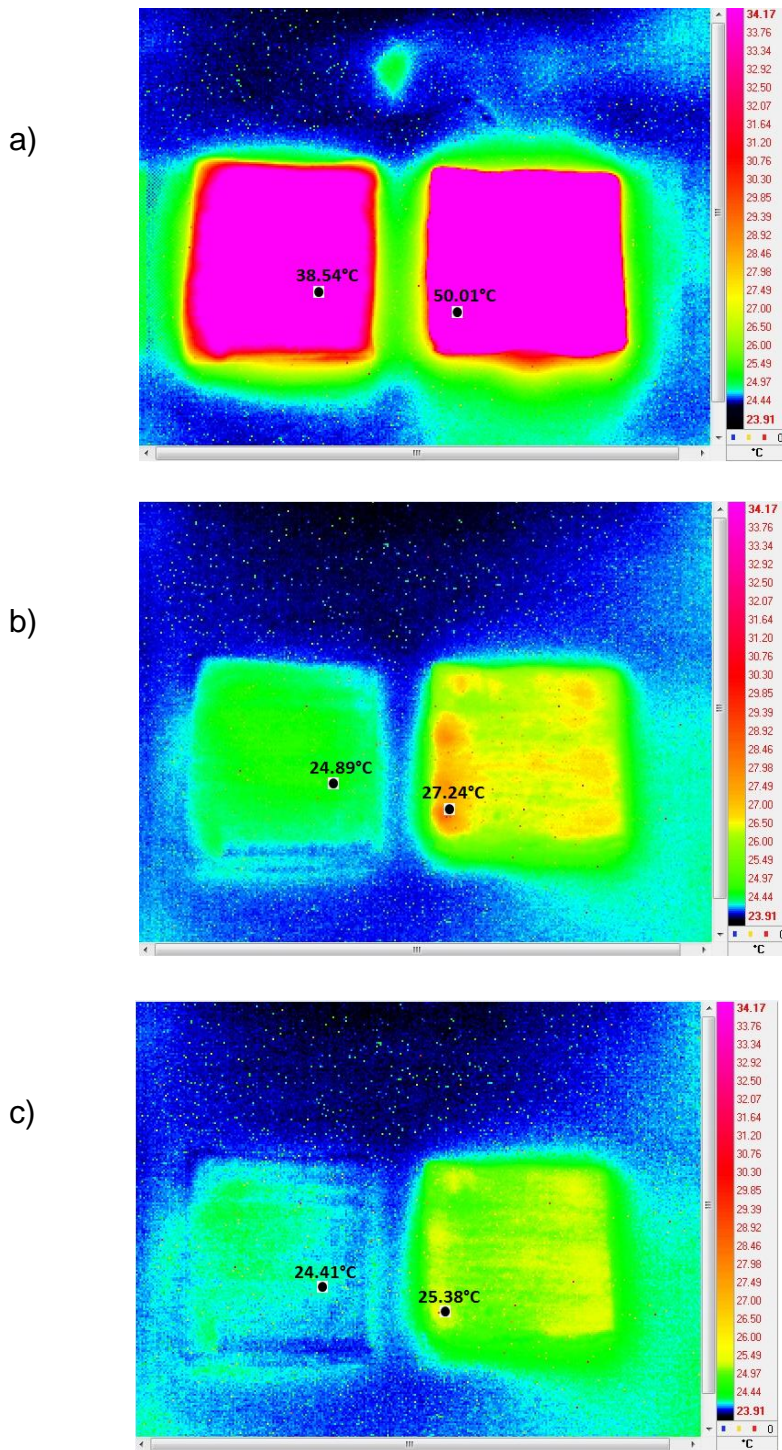


**Figure 59.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC4 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

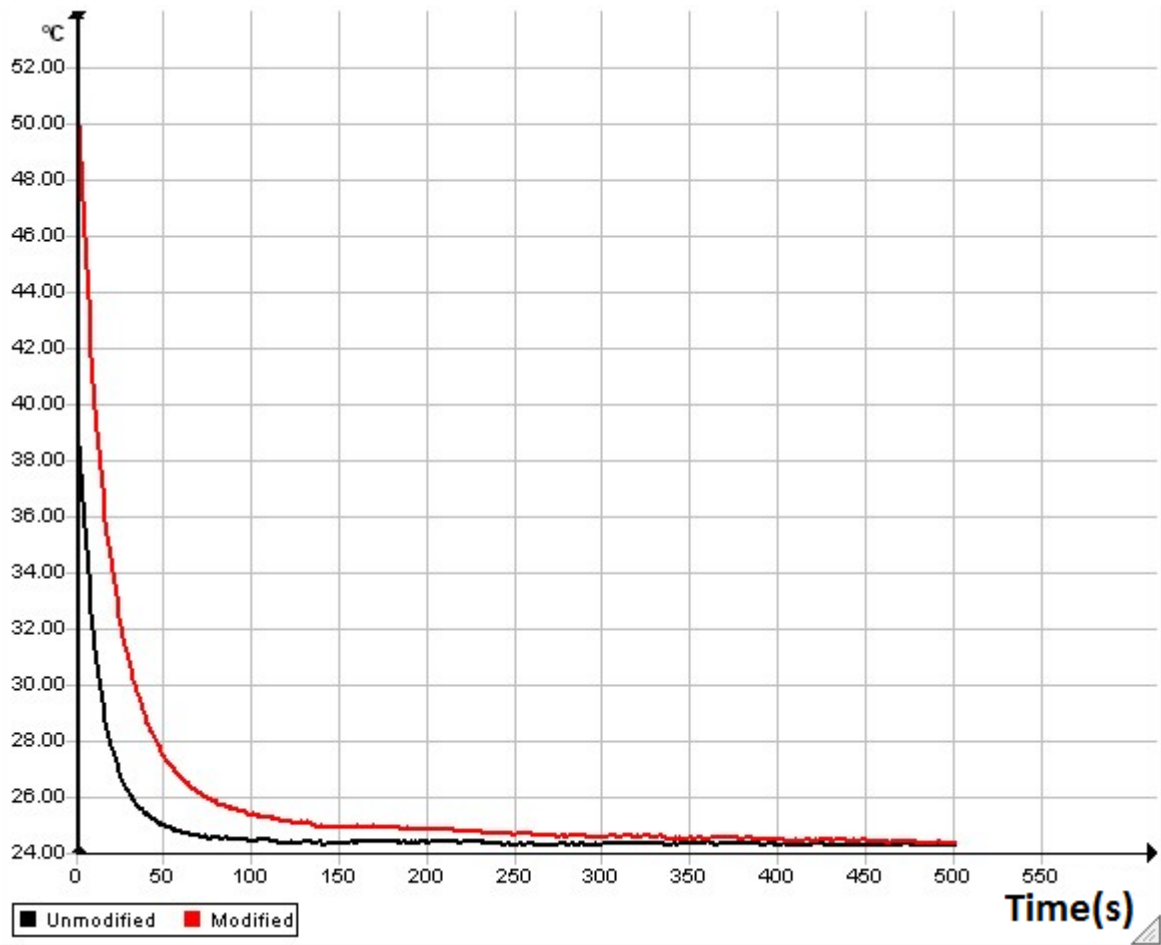


**Figure 60.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BVEC4 microcapsules and chitosan as binder.

## BWPLA4 WITH CHITOSAN.

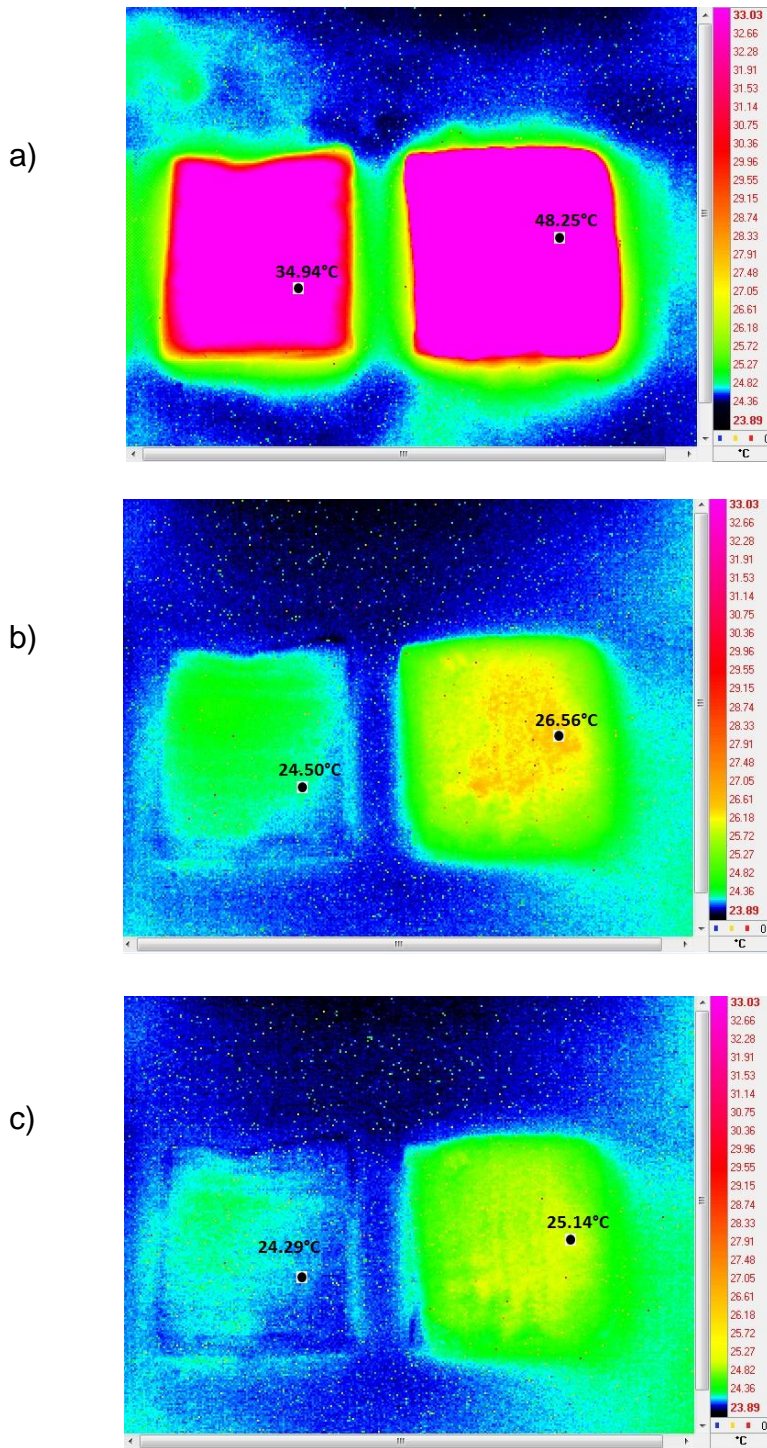


**Figure 61.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWPLA4 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

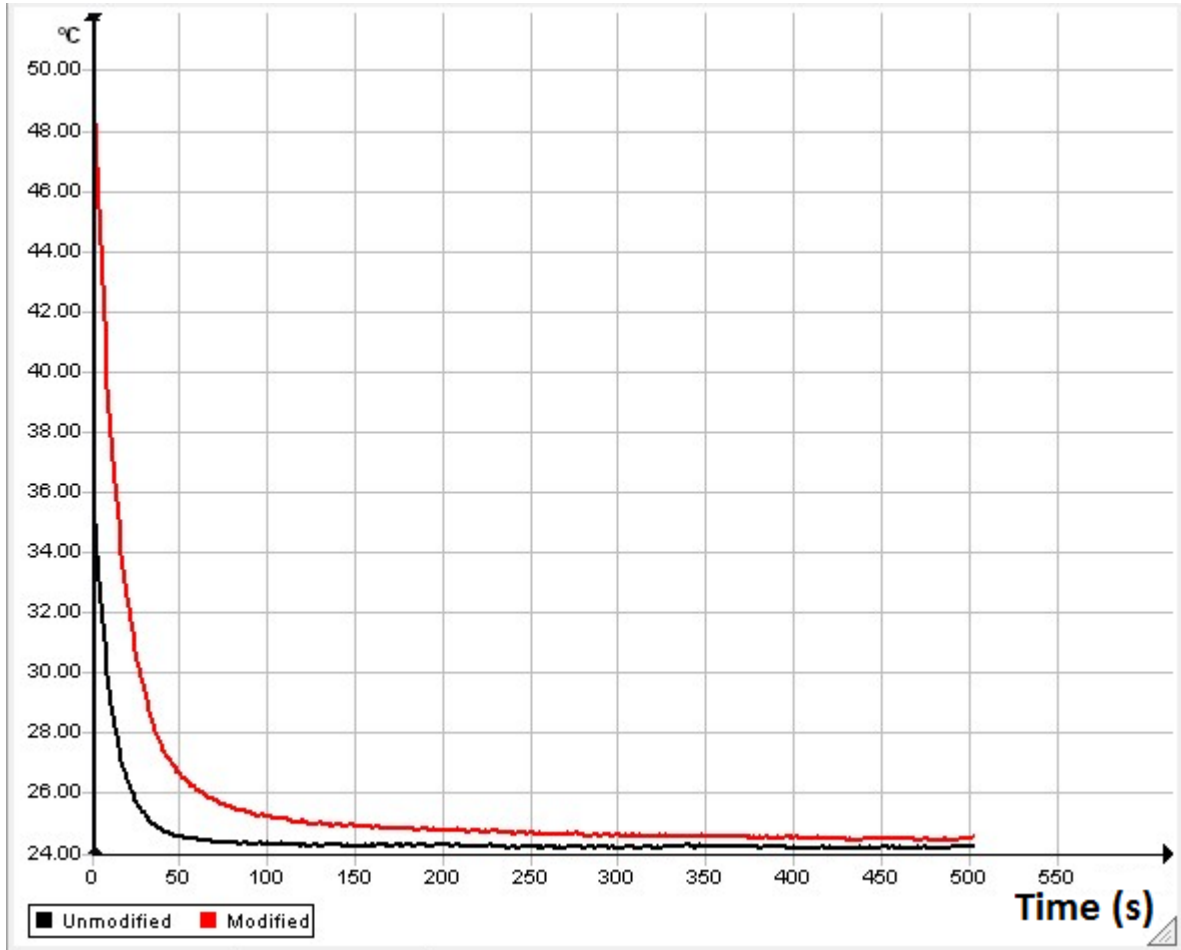


**Figure 62.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWPLA4 microcapsules and chitosan as binder.

**BWEC5 WITH CHITOSAN.**

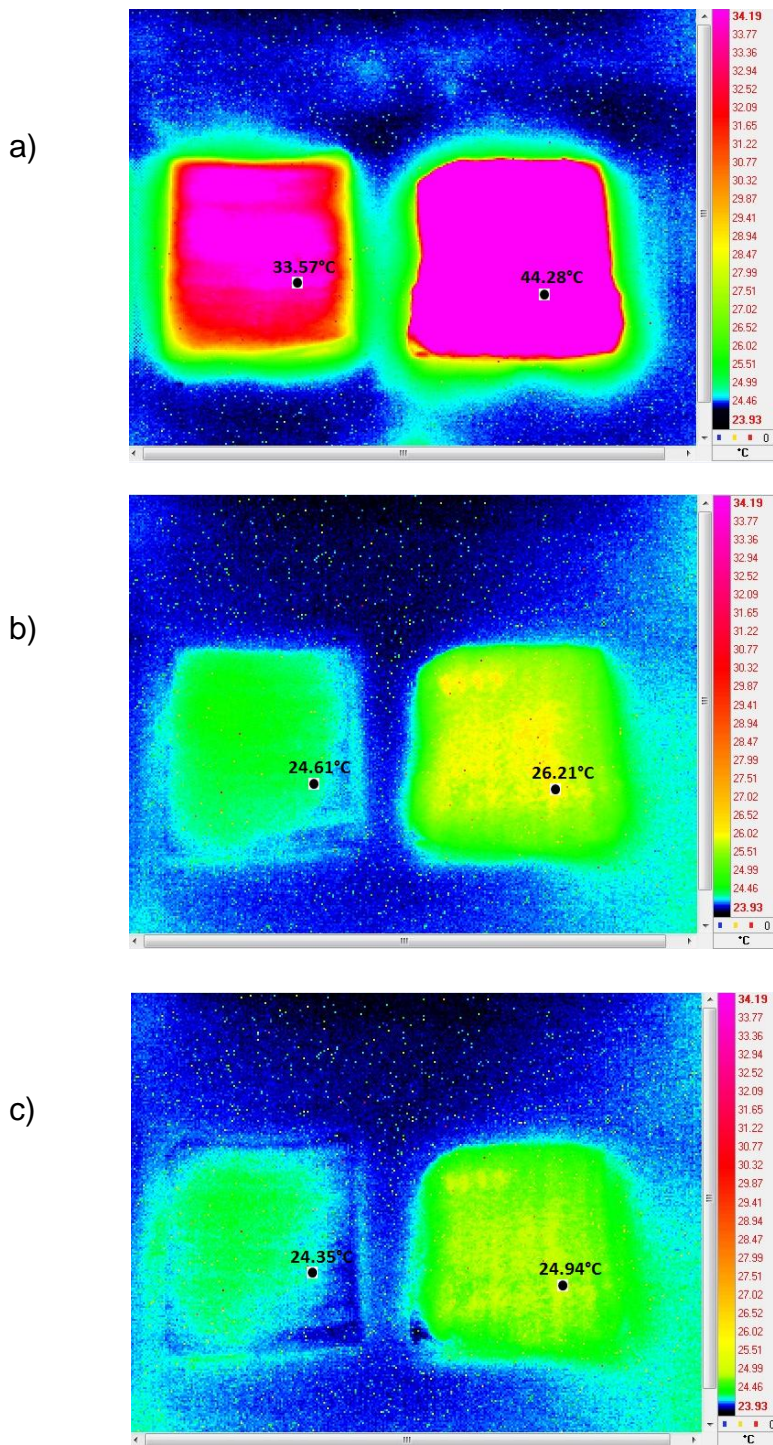


**Figure 63.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC5 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.

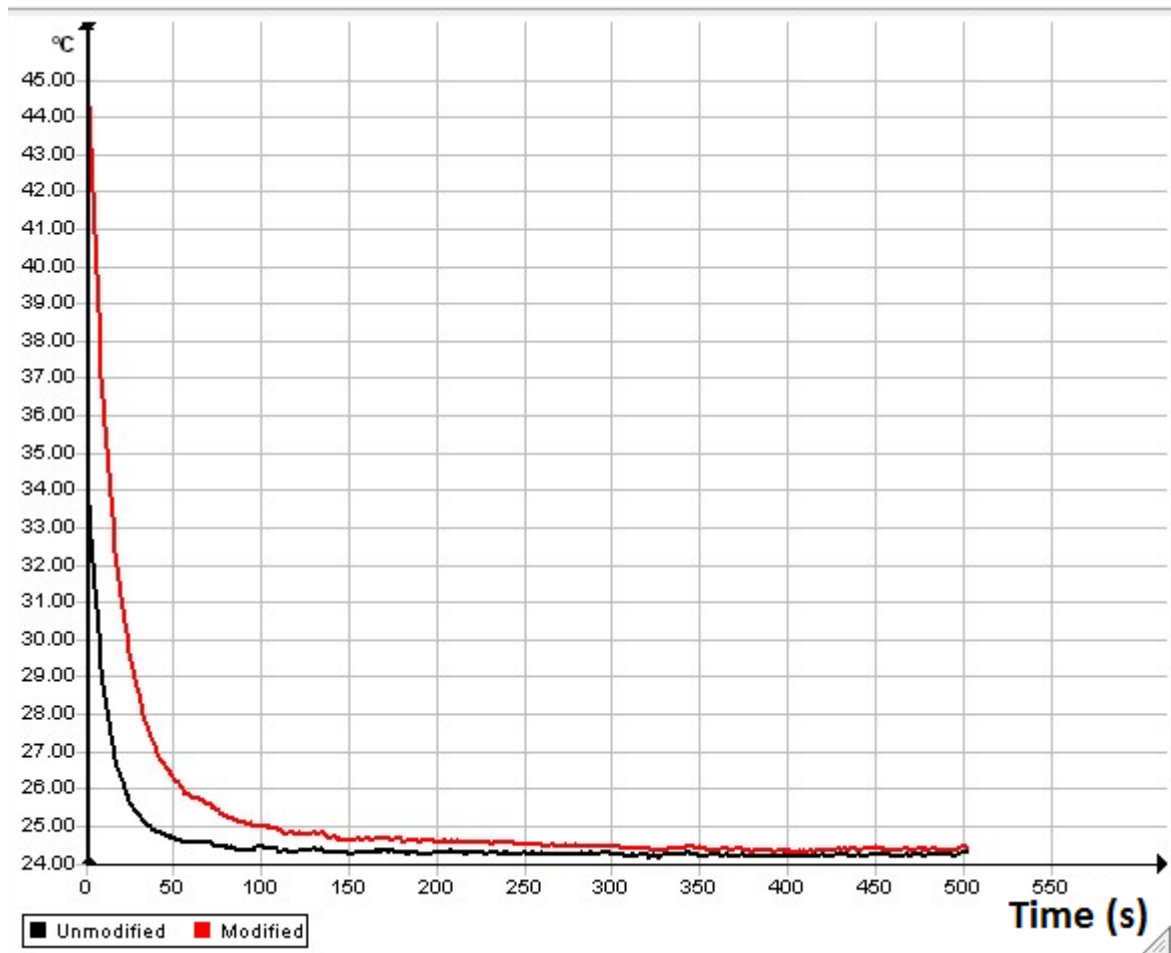


**Figure 64.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC5 microcapsules and chitosan as binder.

## BWEC6 WITH CHITOSAN.



**Figure 65.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC6 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.



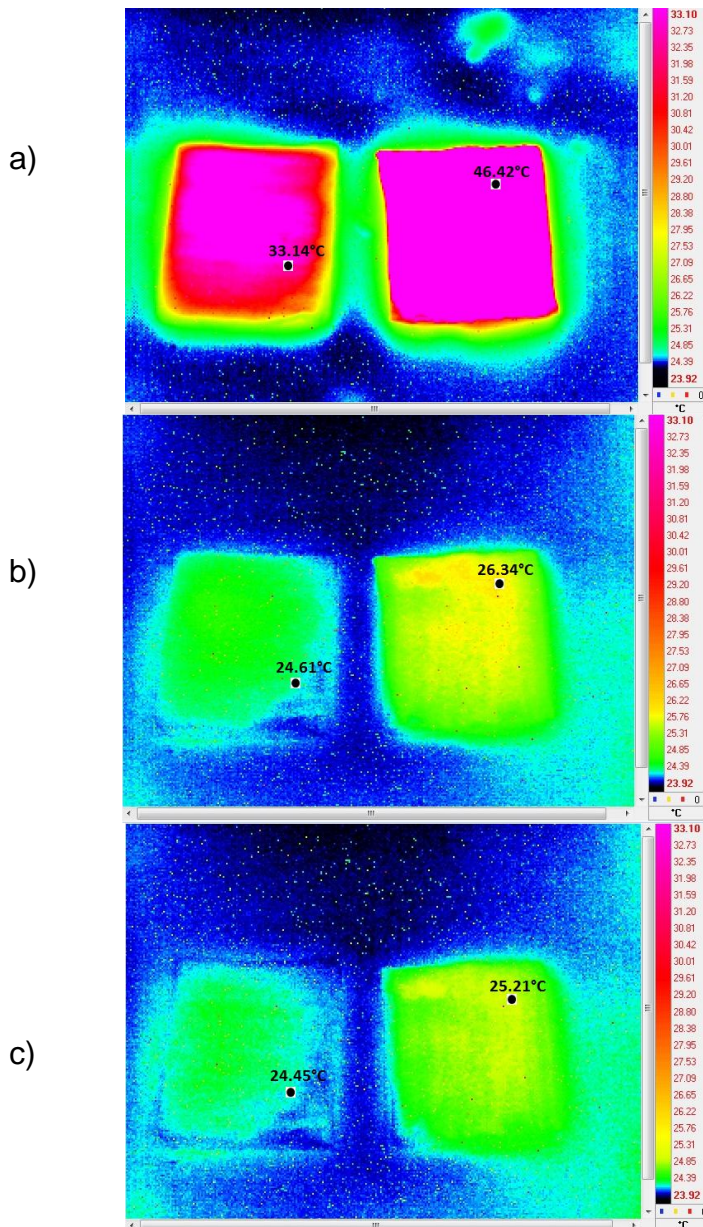
**Figure 66.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC6 microcapsules and chitosan as binder.



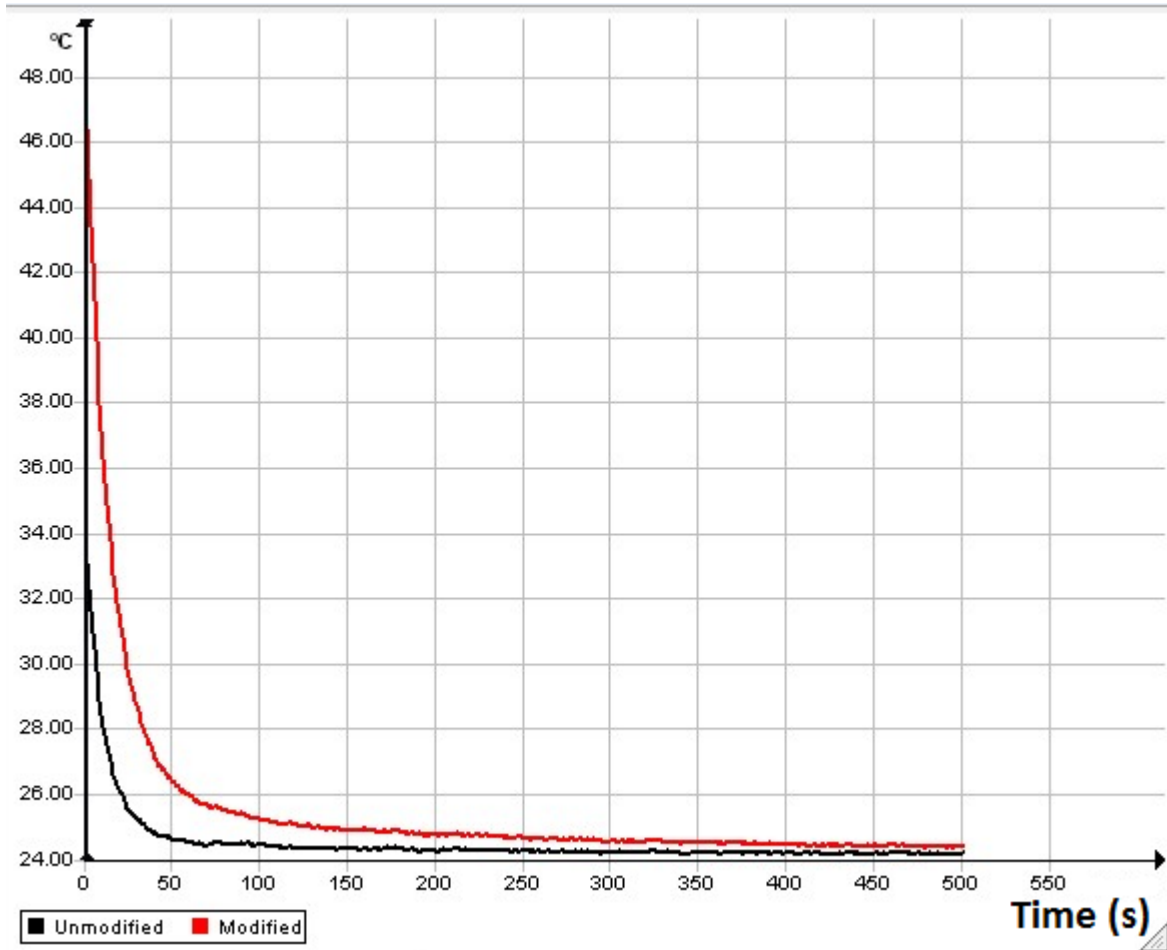
### 5.1.8.3. Modification of textiles with a mix of Bee wax and Coconut Oil microcapsules.

In the following experiment, the bee wax and coconut oil microcapsules were mixed in the same proportion scattered along the textile substrate and the results obtained are presented below.

#### BWEC6 AND COEC3 WITH CHITOSAN.



**Figure 67.** IR images of non-woven PLA unmodified (sample on the left) and modified with BWEC6 and COEC3 (sample on the right) at (a) 0 sec, (b) 50 sec and (c) 100 sec after heating.



**Figure 68.** Timeline graphic of non-woven PLA unmodified and non-woven PLA modified with BWEC6 microcapsules and chitosan as binder.

As you can see in all the graphs the temperature of the unmodified sample decrease faster than the modified sample which means that the modified sample could absorb more heat energy and keep inside for longer time due to the microencapsulated phase change material that it has inside.

The difference between the samples with coconut oil and bee wax microPCMs it can be noticed by the difference of temperature during the first 100 seconds. The difference between the sample modified with bee wax is bigger than the one with coconut oil. The decrease of temperature in samples with coconut oil microPCMs is faster than the one with bee wax due to the bigger latent heat enthalpy that bee wax has.

## 6.0 CONCLUSIONS.

Nowadays many textile applications of PCMs have been studied by many research groups; the important thing in this work is the creation of a new technology of textile PCM application being environmental friendly with 100% biodegradable materials, useful and also inexpensive. Some of the best candidates to develop this work are coconut oil and bee wax as temperature regulator due to their capability to absorb and release large amount of heat energy by changing their phase. It is possible to microencapsulate these two organic PCMs in polylactide (PLA) and ethyl cellulose (EC) as well. PLA as shell material is the best option due to this polymer is enough resistance to the normal situations woven or non-woven textile materials are exposed. Ethyl Cellulose (EC) is also a good option due to its biodegradable properties.

The microcapsules were obtained as a result of interphase precipitation during evaporation of the solvent from water/oil emulsion.

The influence of the type and amount of polymer used as the shell layer, the type and amount of core material, the rate of homogenization or the type of solvent used on the effectiveness of the encapsulation process was investigated.

On the basis of microscopic analysis, microcapsules have a spherical shape regardless of the type of polymer used. If a completely amorphous polymer is used, the microcapsules are characterized by a more porous surface. PLA completely amorphous creates more porous surface microcapsules, besides polymer in form of a film was observed during the process of microencapsulation. That is why PLA with a small proportion of crystalline phase was the most viable option for this procedure.

The influence of the stirring speed was performed at 600 rpm, 900 rpm and 1000 rpm. Reducing the speed of homogenization would increase the viscosity of the dispersed phase, and thereby lead to porous surface of capsules. The microPCMs can have porous in the surface if the solvent evaporates too fast. The most viable solvent is the one that evaporates slower than the others.

The use of a smaller amount of core material allowed to obtain microcapsules with a smoother surface, but at the same time the effectiveness of the capsules was smaller.

The method used to obtain microcapsules allowed to obtain microcapsules with an average diameter of 26  $\mu$ m. This indicates that the microcapsules are tiny and easy to coat onto the fabric surface.

Polylactide and ethyl cellulose microcapsules with coconut oil and bee wax were analyzed by DSC. The melting temperature of pure coconut oil is 25.1°C and in microcapsule form is about the melting temperature of pure bee wax is 55.9°C and in microcapsule form is about 57°C in all cases. The core content of

coconut oil were calculated to be from 18.75 wt% to 38.42 wt%, depending on the type of polymer used and the process conditions . In the case of microcapsules with bee wax, a similar relationship can be observed. The core content in microcapsules were calculated to be from 14.0 wt% to 34.67 wt%.

The microPCMs can be applied manually to the non-woven PLA with the help of a binder which in this case was calcium alginate and chitosan. As it was shown in the SEM images of non-woven PLA with microPCMs applied microcapsules are inside the fabric and stick to it.

The thermal regulating properties of modified textiles were investigated by an IR camera. The results obtained from thermal analysis of samples showed that the temperature of the unmodified sample decreases faster than the modified sample, which means that the modified sample can absorb more thermal energy and stay in it for a longer time due to the microencapsulated phase change material that is inside. Modified nonwovens with microcapsules containing coconut oil or bee wax provide cooling effect, which confirms the effectiveness of the modification.

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